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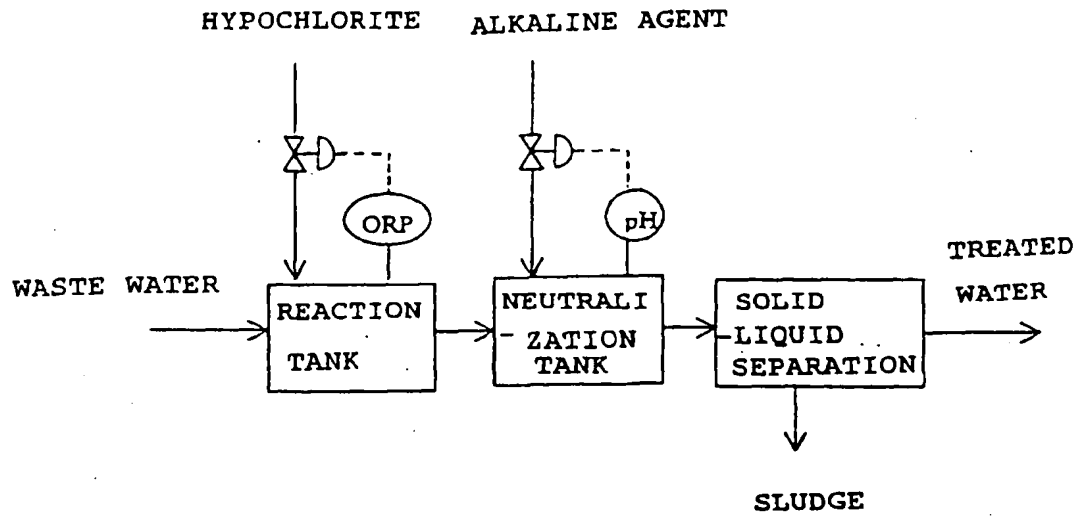
**(54) METHOD FOR FLUE GAS DESULFURIZATION AND FLUE GAS DESULFURIZATION SYSTEM**

(57) The present invention provides a desulfurization waste water treatment method for treating waste water discharged from a wet type flue gas desulfurizer for absorbing and separating sulfur oxide in combustion flue gas by using a wet lime-gypsum process, wherein after hypochlorite is added to the waste water, the pH value is adjusted to 7 to 9.5, and the waste water is subjected to solid-liquid separation; and a flue gas desulfurization method using a wet lime process for treating flue gas containing sulfur oxide and nitrogen oxide, comprising an oxidation process in which the pH value of all or some of filtrate is adjusted to 3 to 4 and an oxidizing agent is added after some of absorbent slurry in a des-

ulfurization process is extracted and gypsum is separated, a neutralization process in which an alkaline agent is mixed with the mixed liquid to adjust the pH value to 7 to 9.5, and a solid-liquid separation process in which the neutralized adjusted liquid is subjected to solid-liquid separation. According to the present invention, NS compounds having an adverse influence on the desulfurization performance can be removed effectively, and at the same time, heavy metals, especially manganese, in desulfurization waste water can be removed favorably in terms of economy as well.

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FIG. 1



**Description**

## TECHNICAL FIELD

5 **[0001]** The present invention relates to a flue gas desulfurization method including the treatment of desulfurization waste water and the treatment of absorbent slurry and a flue gas desulfurization system. More particularly, it relates to a flue gas desulfurization method carried out by a wet lime-gypsum process in which sulfur oxide and nitrogen oxide in flue gas are absorbed and separated by using absorbent slurry of limestone or hydrated lime, a flue gas desulfurization system capable of properly carrying out the above-described method and a treatment method for the above-described absorbent slurry, a method for effecting treatment for making waste water, which is discharged when sulfur oxide gas in combustion flue gas is desulfurized by the wet lime-gypsum process and especially by soot mixing desulfurization treatment, nonpolluting, and the like methods.

## BACKGROUND ART

15 **[0002]** Combustion flue gas produced by combustion using coal or the like as a fuel is treated by using a desulfurizer using the lime-gypsum method, and waste water containing heavy metals such as cadmium and manganese, difficult-to-decompose COD components (components responsible for chemical oxygen demand), and fluorine components is discharged.

20 **[0003]** Conventionally, as a method for removing heavy metals, especially manganese  $Mn^{2+}$ , in desulfurization waste water, there has been available a method for treating heavy metals in an alkaline region of pH 10 to 12. In this method, manganese is precipitated as manganese hydroxide by adjusting pH. Thereby, the quantity of manganese ions in treated water is made 10 mg/L or smaller.

25 **[0004]** With this method, however, magnesium in desulfurization waste water deposits as magnesium hydroxide, so that a large amount of sludge is produced, which presents a problem in that the size of a sludge treatment apparatus increases. Also, because this treated water has a high pH value, pollutants such as fluorine must further be treated on the downstream side, or the pH value must be decreased to a value close to neutrality to meet the effluent regulation standard, which presents a problem of increasing running cost.

30 **[0005]** Conventionally, there has been used a method in which in order to reduce a large amount of sludge such as deposited magnesium hydroxide, the sludge is absorbed in gypsum. In this method, however, the hydroxide is mixed with desulfurization gypsum and is dehydrated, so that the operation control of a gypsum separator becomes difficult to accomplish, and at the same time, an adverse influence on the water content and purity of the obtained gypsum is brought about.

35 **[0006]** Further, as a method for removing  $Mn^{2+}$  in desulfurization waste water, there has been disclosed a method for removing it as manganese dioxide by adding permanganate to adjust the pH to 3 to 8. However, the use of expensive permanganate poses a problem of increasing running cost.

40 **[0007]** On the other hand, the difficult-to-decompose COD components contained in desulfurization waste water include inorganic COD components and organic COD components. The inorganic COD components consist of nitrogen-sulfur compounds (hereinafter referred to as "N-S compounds") yielded by the reaction of  $SO_2$  absorbed in the absorbent in the desulfurizer with some of  $NO_x$ . Also, the organic COD components consist mainly of organic components in industrial water used as make-up water for the desulfurizer.

**[0008]** These COD components have difficulty in being removed by a coagulative precipitation method using an ordinary coagulant or by an activated sludge method using microorganism, so that it is very difficult to attain the effluent standard (for example, 20 mg/L or less) of COD components.

45 **[0009]** As a method for decomposing N-S compounds of the above-described COD compounds, a method for decomposing nitrite ( $NO_2^-$ ) has been known well. With this method, sodium nitrite is added in a fixed ratio, and decomposition is effected under conditions of pH of 2 and less and a temperature of 45°C and higher.

50 **[0010]** The discharged desulfurization waste water is usually neutral or weakly acidic, so that a large amount of acid is needed to provide pH of 2 and less. Moreover, a large amount of alkaline agent is needed to restore the neutrality or weak alkalinity after the reaction has been finished. Therefore, there arises a drawback in that wasteful cost for chemicals and much manpower are required.

**[0011]** Also, there is available a method in which after some of absorbent slurry in the desulfurizer is extracted and is subjected to solid-liquid separation, the pH value of separated liquid (filtrate) is adjusted to be 3 to 4 and hypochlorite is added, by which N-S compounds are removed. With this treatment method, the N-S compounds in treated water can be removed to a level of 5 mg/L (milligram/liter) and less of COD.

55 **[0012]** However, although the N-S compounds in desulfurization waste water can be treated by this treatment method, a method for collectively treating coexistent components such as manganese and other heavy metals and organic COD components has not yet been studied. Moreover, the organic-COD components contained in desulfurization

waste water are also very difficult to decompose. Therefore, there arises a problem in that in order to sufficiently adsorb and remove the organic components, the size of adsorption facility must be increased.

[0013] As described above, as the treatment method for COD components, there are available the coagulative precipitation method using an ordinary coagulant and the activated sludge method using microorganism. Also, as the method for decomposing N-S compounds, the nitrite decomposing method has been known well. However, from the viewpoint of the cost of chemicals and the workability, a method has also been known in which after some of absorbent slurry in the desulfurizer is extracted and is subjected to solid-liquid separation, the pH value of separated liquid (filtrate) is adjusted and an oxidizing agent is added, by which N-S compounds are removed.

[0014] In the treatment method for desulfurization waste water, in addition to the treatment of N-S compounds in desulfurization waste water, coexistent components such as other organic COD, fluorine, and heavy metals must be treated.

[0015] Because the organic COD components contained in desulfurization waste water are difficult to decompose, as a treatment method for difficult-to-decompose organic COD components, an activated charcoal adsorption method has generally been used. However, the adsorbing property to activated charcoal is very low. Therefore, in order to sufficiently adsorb and remove the organic components, the size of adsorption facility must be increased.

[0016] Also, as a treatment method for waste water containing fluorine, a calcium coagulative precipitation method in which fluorine is removed as calcium fluoride by adding calcium ions to fluorine ions has generally been used, and as a treatment method that is an improvement on the above-described method, a two-stage coagulative precipitation method is well known. In this method, after precipitate consisting of hydroxides etc. of heavy metals yielded by the addition of hydrated lime is once removed, an alkaline agent such as sodium hydroxide is added to yield an alkaline region, by which magnesium ions are deposited as precipitate of magnesium hydroxide (hydroxide), and at the same time, the remaining fluorine ions are co-precipitated and separated.

[0017] Such conventional treatment methods have a problem in that the desulfurization waste water treatment process for flue gas desulfurization is large in scale and complicated, and the process produces a large amount of wastes.

[0018] Also, conventionally, some of filtrate after the separation of gypsum has been treated as waste water by the COD treatment, separation by coagulative precipitation, activated charcoal treatment, fluorine treatment, and the like, and studies have been made as the treatment method for desulfurization waste water, so that complicated post-treatment is necessary.

[0019] Specifically, in the prior art, absorbent slurry flows from the desulfurizer to a gypsum separator directly, and gypsum is removed by the gypsum separator. However, the filtrate contains heavy metals and other components. After the gypsum separation process, some of the filtrate is extracted as waste water to a filtrate treatment process, and processes of COD decomposition, coagulative precipitation by the addition of a heavy metal chelating agent, activated charcoal adsorption, and fluorine adsorption are carried out in succession. By such complicated treatment in the post-treatment process, heavy metals can be separated and removed. On the other hand, if the filtrate is separated after the separation of gypsum, SS components are always produced as sludge in the subsequent waste water treatment process. The cost for treating a large amount of sludge is high, so that this treatment method is disadvantageous in terms of cost.

[0020] Therefore, in the conventional plant, a method can be used in which in order to decrease the amount of sludge coming from the waste water treatment, the sludge is mixed again at the preceding stage of the gypsum separation process, in other words, in order to decrease the amount of discharged sludge, the sludge coming from the waste water treatment is further contained in gypsum. In this method, all solid content (hydroxide, etc.) yielded by the separation of SS components effected by coagulative separation etc. is mixed with absorbent slurry after the desulfurization process and is mixed in gypsum.

[0021] However, in the case where the sludge after coagulative precipitation is returned to the preceding stage of the gypsum separation by this method, if the returned matter is hydroxide, the amount of sludge increases, or the operation control of the gypsum separator at the time of dehydration becomes difficult and complicated. That is to say, since the hydroxide yielded by the desulfurization waste water treatment process is mixed with desulfurization gypsum and is dehydrated, the operation control of the gypsum separator becomes difficult to accomplish, and at the same time, an adverse influence on the water content and purity of the obtained gypsum is liable to be brought about.

[0022] As described above, in the waste water treatment that is conducted for some filtrate after gypsum separation, sludge mainly containing SS components and wastes containing heavy metals etc. contained in waste water are sent together, so that various complicated processes are needed for the treatment.

[0023] On the other hand, in the waste water treatment process after the gypsum separation process, a process in which a heavy metal chelating agent, a coagulation assistant, permanganate, or the like is added to the filtrate has so far been conducted. For the above-described treatment process, for example, the desulfurization process and the waste water treatment process have undergone technical development independently.

[0024] Therefore, a thorough study has not been made on whether the treatment can be promoted as the whole system, the treatment facility can be simplified, and the quantity of sludge can be decreased by efficiently combining

the desulfurization process and the waste water treatment process.

#### DISCLOSURE OF THE INVENTION

**[0025]** Accordingly, a first object of the present invention is to remove heavy metals, especially manganese, in desulfurization waste water while solving problems with the above-described prior art.

**[0026]** To achieve the above object, a first invention of the present invention provides a desulfurization waste water treatment method in which after hypochlorite is added to waste water, which has been discharged from a wet type flue gas desulfurizer for absorbing and separating sulfur oxide in combustion flue gas by using a wet lime-gypsum process, the pH value is adjusted to 7 to 9.5, and the waste water is subjected to solid-liquid separation.

**[0027]** Also, this invention provides a desulfurization waste water treatment method in which after hypochlorite is added to waste water, the pH value is adjusted to 7 to 9.5, and the waste water is subjected to solid-liquid separation after sulfite or bisulfite and a heavy metal chelating agent are added.

**[0028]** In the method in accordance with the present invention, the hypochlorite is preferably added so that the oxidation-reduction potential is 600 mV and higher. Also, the sulfite or bisulfite is preferably added so that the oxidation-reduction potential is 200 mV and higher.

**[0029]** In the method in accordance with the present invention, the liquid to which the sulfite or bisulfite is added can be agitated by air. Also, as the solid-liquid separation method, a microfiltration membrane separation method can be used. In the microfiltration membrane separation, filtrate is preferably agitated by air.

**[0030]** According to the present invention, not only waste water discharged from a wet type flue gas desulfurizer for absorbing and separating sulfur oxide in combustion flue gas by using a wet lime-gypsum process, but also waste water etc. containing heavy metals, especially manganese, can be treated.

**[0031]** In the waste water treatment method in accordance with the present invention, not only manganese and other heavy metals can be removed efficiently by using a simple apparatus, but also the concentration of manganese in the treated water can be made low and stable.

**[0032]** Also, since waste water is treated in a neutral or weakly alkaline environment having a pH value of 9.5 and lower, for example, 7 to 9.5, in which magnesium ions do not turn into magnesium hydroxide, the quantity of produced sludge is small, which is economical.

**[0033]** A second object of the present invention is to, in view of the above-described problems, develop a system in which the treatment efficiency in a desulfurization process and a waste water treatment process in the flue gas desulfurization system can be enhanced, and also the quantity of sludge discharged by the treatment can be decreased.

**[0034]** The inventors found that the problems can be solved by effectively combining the desulfurization process and the waste water treatment process into a unit in the flue gas desulfurization system. The present invention was completed from this point of view. According to the present invention, components such as difficult-to-decompose COD components, heavy metals, and fluorine can be removed efficiently and sufficiently from absorbent slurry of the wet type flue gas desulfurizer for coal combustion flue gas, and also the desulfurizer can be operated efficiently and waste water can be treated easily while preventing sludge from being produced in the waste water treatment.

**[0035]** To achieve the above object, a second invention of the present invention provides an absorbent slurry treatment method for treating absorbent slurry in which sulfur oxide gas in flue gas is absorbed, wherein after a mixing process in which a heavy metal chelating agent is added to and mixed with the absorbent slurry, there are provided a gypsum separation process in which gypsum is separated, an oxidation process in which an oxidizing agent is added to filtrate coming from the gypsum separation process, and a membrane separation process in which liquid coming from the oxidation process is filtrated by using a separation membrane. For example, in one mode, as the absorbent slurry, slurry in which sulfur oxide gas is absorbed in the desulfurization process is used, and some of the liquid having been subjected to the gypsum separation process and oxidation process is returned to the desulfurization process as concentrate.

**[0036]** In the above-described treatment method, in addition to the processes described above, there can be provided an activated charcoal adsorption process in which membrane filtrate subjected to the membrane separation process is brought into contact with activated charcoal and a fluorine adsorption process in which treated liquid coming from the activated charcoal adsorption process is brought into contact with a fluorine adsorption resin. There is also provided a mode in which in the mixing process, a solidifying substance such as permanganate is added in addition to the heavy metal chelating agent.

**[0037]** The heavy metal chelating agent is preferably dithiocarbamic acid group or thiol group or both of them. The treated liquid coming from the oxidation process preferably goes to the membrane separation process after being treated in a neutralization process in which a reducing agent is added. As the oxidizing agent, for example, hypochlorite is preferable. Also, as the reducing agent, a flue gas or the like can be used.

**[0038]** For the treatment method in accordance with the present invention, a mode is preferably used in which a solid substance separated in the membrane separation process is returned to the mixing process, and sent to the gypsum

separation process after being mixed with the absorbent slurry, or a mode is preferably used in which recycled waste liquid in the fluorine adsorption process is returned to the desulfurization process.

[0039] Also, the present invention provides a flue gas desulfurization system using a wet lime-gypsum process in which sulfur oxide gas in flue gas is absorbed and separated by using absorbent slurry of limestone or hydrated lime, comprising a mixing tank in which a heavy metal chelating agent is added to and mixed with the absorbent slurry, a gypsum separator for separating gypsum, an oxidation tank in which hypochlorite is added to filtrate from which gypsum is separated, and a membrane separation tank in which liquid coming from the oxidation process is filtrated. The above-described flue gas desulfurization system can comprise, in addition to the elements described above, an activated charcoal adsorption tower in which filtrate coming from the membrane separation process is brought into contact with activated charcoal and a fluorine adsorption tower in which treated liquid coming from the activated charcoal adsorption tower is brought into contact with a fluorine adsorption resin. There is also provided a mode in which in the mixing tank, a solidifying substance such as permanganate is added in addition to the heavy metal chelating agent. Further, there is also provided a mode in which a neutralization tank in which a reducing agent is added to treated liquid coming from the oxidation tank is provided between the oxidation tank and the membrane separation tank.

[0040] The separation membrane is preferably a tubular type microfiltration membrane, a submerged type flat-plate microfiltration membrane, or a submerged type hollow-fiber microfiltration membrane. The fluorine adsorption resin is preferably a zirconium carrier type resin or a cesium carrier type resin.

[0041] A mode is preferably used in which in the flue gas desulfurization system in accordance with the present invention, the membrane separation tank and the neutralization tank are installed in an absorption tower of the desulfurizer.

[0042] The absorbent slurry to be treated in the present invention, which is slurry in which sulfur oxide gas in flue gas is absorbed by using limestone or hydrated lime, contains COD components, heavy metals, fluorine, and the like in addition to sulfur oxide.

[0043] In the present invention, by effectively combining the treatment process and desulfurization process (desulfurizer) into a unit in the treatment process, wastes etc. containing heavy metals are mixed with desulfurization gypsum to reduce wastes requiring complicated treatment, and the quantity of finally treated wastes discharged as sludge is decreased. Also, the treatment process is made as simple as possible, by which the desulfurization process and the waste water treatment process can be carried out efficiently as a unit.

[0044] In the present invention, some treatment processes that have so far been carried out for waste water treatment are carried out immediately after the desulfurization process, by which the whole treatment is promoted and is made efficient. After the mixing tank in which the chelating agent is added, the gypsum separation process (solid content separation), the oxidation process (COD decomposition process), and the membrane separation process (solid content separation process) are carried out in this order.

[0045] According to the present invention, the quantity of deposited sludge is far smaller than the quantity of by-product gypsum, and sludge is hardly produced. Also, since no hydroxide is produced in the waste water treatment, the hydroxide need not be mixed with gypsum, so that the water content and purity of gypsum are not influenced adversely.

[0046] Also, by using the separation process using the separation membrane in place of the conventional coagulative separation process, sand filtration process, and the like, the treatment process can be simplified, and also the increased size of equipment and the necessity of a large-scale treatment facility can be avoided.

[0047] A third object of the present invention is to, in view of the above-described problems, develop a flue gas desulfurization method or system in which NS compounds having an adverse influence on the desulfurization performance can be removed effectively, and at the same time, heavy-metals, especially manganese, in desulfurization waste water can be removed favorably in terms of economy as well.

[0048] The inventors found that the problems can be solved by a treatment method in which after gypsum separation, the pH value of filtrate is adjusted to 3 to 4 and an oxidizing agent such as hypochlorite is added, and after neutralization, liquid is subjected to solid-liquid separation, in the flue gas desulfurization method.

[0049] To achieve the above object, a third invention of the present invention provides a flue gas desulfurization method using a wet lime process for treating flue gas containing sulfur oxide and nitrogen oxide, comprising an oxidation process in which the pH value of all or some of filtrate is adjusted to 3 to 4 and an oxidizing agent is added after some of absorbent slurry in a desulfurization process is extracted and gypsum is separated, a neutralization process in which an alkaline agent is mixed with the mixed liquid to adjust the pH value to 7 to 9.5, and a solid-liquid separation process in which the neutralized adjusted liquid is subjected to solid-liquid separation. There is also provided a mode in which after a heavy metal chelating agent is added to some of the absorbent slurry extracted from the desulfurization process, gypsum is separated.

[0050] The solid-liquid separation is preferably effected by membrane separation. Some of solid substance concentrate yielded by the solid-liquid separation can be mixed with the absorbent slurry to be subjected to solid-liquid separation or can be supplied to the absorption tower as make-up water.

[0051] Also, filtrate subjected to the solid-liquid separation can be discharged to the outside of the system as waste water. In the neutralization process, sulfite or sulfurous acid gas is preferably added.

[0052] Further, the present invention provides a flue gas desulfurization system using a wet lime process for treating flue gas containing sulfur oxide and nitrogen oxide, wherein on the downstream side of a gypsum separator for separating gypsum from absorbent slurry introduced from an absorption tower, there are provided an oxidation tank in which the pH value of all or some of filtrate from which gypsum has been separated is adjusted to 3 to 4 and an oxidizing agent is added, a neutralization tank in which an alkaline agent is mixed with the liquid coming from the oxidation tank to adjust the pH value to 7 to 9.5, and a membrane separation tank in which the liquid coming from the neutralization tank is subjected to solid-liquid separation by using a membrane.

[0053] In the system in accordance with the present invention, there is preferably used a mode in which the oxidation tank, neutralization tank, and membrane separation tank on the downstream side of the gypsum separator are arranged vertically as a unit under the gypsum separator so that fluid flows down from the gypsum separator to the oxidation tank, from the oxidation tank to the neutralization tank, and from the neutralization tank to the membrane separation tank in succession, or a mode in which the oxidation tank, neutralization tank, and membrane separation tank are arranged vertically under the gypsum separator so that fluid flows down from the gypsum separator to the oxidation tank and from the neutralization tank to the membrane separation tank in succession. Some of solid substance concentrate yielded by the solid-liquid separation can be mixed with the absorbent slurry to be subjected to solid-liquid separation, or can be supplied to the absorption tower as make-up water. Also, filtrate subjected to the solid-liquid separation can be discharged to the outside of the system as waste water.

[0054] In the present invention, N-S compounds having an influence on the desulfurization performance are removed, by which an adverse influence on the desulfurization performance can be avoided.

[0055] According to the present invention, since the quantity of deposited sludge is far smaller than the quantity of by-product gypsum, and sludge is hardly produced, even if solid substance concentrate is sent again to the preceding stage of the gypsum separator, the water content and purity of gypsum are not influenced adversely.

[0056] Also, when sodium hypochlorite or the like is used as an oxidizing agent, because it is an inexpensive chemical, the running cost is low.

[0057] Further, N-S compounds, which are difficult-to-decompose COD, and manganese ions  $Mn^{2+}$  can be treated efficiently at the same time, and the burden on the waste water treatment can be alleviated, so that the waste water treatment system can be simplified. According to the present invention as described above, waste water etc. containing heavy metals, especially manganese, discharged from the wet type flue gas desulfurizer can be treated, so that the concentration of manganese in the treated water is low and stable.

#### BRIEF DESCRIPTION OF THE DRAWINGS

[0058]

FIG. 1 is a system diagram of one embodiment of a waste water treatment method in accordance with a first invention of the present invention;

FIG. 2 is a system diagram of another embodiment of a waste water treatment method in accordance with the first invention of the present invention;

FIG. 3 is a system diagram of still another embodiment of a waste water treatment method in accordance with the first invention of the present invention;

FIG. 4 is a configuration diagram schematically showing one example of a flue gas desulfurization system in accordance with a second invention of the present invention;

FIG. 5 is a configuration diagram schematically showing another example of a flue gas desulfurization system in accordance with the second invention of the present invention;

FIG. 6 is a configuration diagram schematically showing still another example of a flue gas desulfurization system in accordance with the second invention of the present invention;

FIG. 7 is a configuration diagram schematically showing still another example of a flue gas desulfurization system in accordance with the second invention of the present invention;

FIG. 8 is a system diagram showing one example of a system for carrying out a flue gas desulfurization method in accordance with a third invention of the present invention;

FIG. 9 is a system diagram showing another example of a system for carrying out a flue gas desulfurization method in accordance with the third invention of the present invention;

FIG. 10 is a system diagram showing still another example of a system for carrying out a flue gas desulfurization method in accordance with the third invention of the present invention;

FIG. 11 is a system diagram showing still another example of a system for carrying out a flue gas desulfurization method in accordance with the third invention of the present invention;

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FIG. 12 is a system diagram showing still another example of a system for carrying out a flue gas desulfurization method in accordance with the third invention of the present invention; and

FIG. 13 is a system diagram showing still another example of a system for carrying out a flue gas desulfurization method in accordance with the third invention of the present invention.

[0059] In the above figures, reference numeral 1 denotes a desulfurizer, 2 denotes a circulating pump, 3 denotes absorbent slurry, 4 denotes a mixing tank, 5 denotes a heavy metal chelating agent, 6 denotes a coagulation assistant, 7 denotes permanganate, 8 denotes mixed liquid, 9 denotes a gypsum separator, 10 denotes gypsum, 10a denotes gypsum cake, 11 denotes filtrate, 12 denotes an oxidation tank, 13 denotes acid, 14 denotes hypochlorite, 15 denotes an oxidation reaction tank, 16 denotes a neutralization tank, 17 denotes alkali, 18 denotes a reducing agent, 19 denotes neutralization reaction liquid, 20 denotes a membrane separation tank, 21 denotes a separation membrane, 22 denotes air, 23 denotes an air-diffusing pipe, 24 denotes a concentrate pump, 25 denotes concentrate, 26 denotes a precipitate pump, 27 denotes precipitate slurry, 28 denotes membrane filtrate (membrane separation liquid), 29 denotes a receiver, 30 denotes a vacuum pump, 31 denotes flue gas, 32 denotes a membrane separation liquid tank, 33 denotes an activated charcoal pump, 34 denotes an activated charcoal adsorption tank, 35 denotes activated charcoal treated water, 36 denotes an activated charcoal treated water tank, 37 denotes a fluorine adsorption tower pump, 38 denotes a fluorine adsorption tower, 39 denotes fluorine treated water, 40 denotes a treated water tank, 41 denotes treated water, 42 denotes recycled waste liquid, 43 denotes a recycled waste liquid tank, 44 denotes a recycled waste liquid pump, 101 denotes flue gas, 102 denotes an absorption tower, 103 denotes outlet gas, 104 denotes a slurry tank, 105 denotes an absorbent pump, 106 denotes an oxidizing air supply line, 107 denotes an absorbent slurry draw line, 108 denotes a gypsum separator, 109 denotes gypsum, 110, 110a, and 110b denote filtrate, 111 denotes an oxidation tank, 112 denotes acid, 113 denotes an oxidizing agent, 114 denotes alkali, 115 denotes a reducing agent ( sulfite, sulfurous acid gas, or bisulfite) , 116 denotes a neutralization tank, 117 denotes a membrane separation tank, 118 denotes a separation membrane, 119 denotes a vacuum pump, 120 denotes a receiver, 121 denotes membrane filtrate, 122 denotes a solid substance concentrate pump, 123 denotes solid substance concentrate, 124 denotes overflow water, 125 denotes a limestone preparation tank, 126 denotes limestone, 127 denotes a limestone slurry supply pump, 130 denotes a mixing tank, and 131 denotes a heavy metal chelating agent.

### BEST MODE FOR CARRYING OUT THE INVENTION

[0060] Embodiments of the present invention will now be described with preference to the accompanying drawings.

#### Embodiment of first invention

[0061] One example for carrying out a method in accordance with a first invention of the present invention will be described with reference to FIG. 1. The present invention is not limited to this embodiment.

[0062] In the present invention, after hypochlorite is added to desulfurization waste water, the pH value is adjusted to 7 to 9.5, and solid-liquid separation is effected to remove manganese in the desulfurization waste water.

[0063] In the desulfurization waste water treatment method in accordance with the present invention, hypochlorite is first added to waste water having been introduced into a reaction tank and the waste water is mixed. As hypochlorite, sodium hypochlorite, bleaching powder, and the like can be used, and sodium hypochlorite is preferably used from the viewpoint of handling.

[0064] The pH value of desulfurization waste water is usually in an acidic region, and in the case where an oxidizable substance such as an organic substance is present in the waste water, when the waste water is mixed with hypochlorite, hypochlorite is consumed by the oxidation. Therefore, as a necessity for oxidation of the oxidizable substance and manganese ions, hypochlorite is added so that the oxidation-reduction potential in the reaction tank is 600 mV and higher, preferably 700 to 900 mV. If the oxidation-reduction potential is lower than this range, the oxidation of manganese ions is insufficient, and if it is higher than this range, the addition of hypochlorite becomes excessive, so that the consumption of chemicals increases undesirably.

[0065] Next, the reaction liquid of the reaction tank is introduced into a neutralization tank. In the neutralization tank, an alkaline agent is added so that the pH value is 7 to 9.5. As the alkaline agent, sodium hydroxide, calcium hydroxide, potassium hydroxide, or the like can be used. Of these compounds, calcium hydroxide increases the quantity of sludge, and potassium hydroxide is expensive, causing a poor economy. Therefore, considering economical efficiency and convenience in handling, sodium hydroxide is preferable.

[0066] In the neutralization tank, manganese ions are turned into manganese dioxide by the alkaline agent, and the manganese dioxide deposits as a soluble solid content. However, since the pH value is adjusted to 7 to 9.5 in the neutralization tank, magnesium hydroxide does not deposit.

[0067] Next, the reaction liquid of the neutralization tank is introduced into a solid-liquid separator. As solid-liquid

separation means, a conventional coagulative precipitation method can be used. In this case, a high molecular coagulant is preferably added to the reaction liquid at the outlet of the neutralization tank (not shown) to facilitate the formation and precipitation of coagulated flocks. A supernatant liquid of the precipitation tank is discharged to the outside of the system as treated water, and precipitated solid substances including manganese dioxide are discharged as sludge.

**[0068]** In some cases, unreacted hypochlorite remains in the treated water. Therefore, sulfite or bisulfite is preferably added to the treated water to remove residual chlorine.

**[0069]** The method shown in FIG. 1 can be applied to the case of desulfurization waste water in which the concentration of heavy metals other than manganese poses no problem. The characters of ORP in the figure denote means for measuring oxidation-reduction potential, and pH denotes means for measuring pH value.

**[0070]** FIG. 2 shows another example for carrying out the first invention of the present invention.

**[0071]** In this method, hypochlorite is first added to waste water having been introduced into a reaction tank and the waste water is mixed. In this case as well, as in the method shown in FIG. 1, hypochlorite is added so that the oxidation-reduction potential in the reaction tank is 600 mV and higher, preferably 700 to 900 mV.

**[0072]** Next, the reaction liquid of the reaction tank is introduced into a neutralization tank. At this time, after an alkaline agent is poured into an introduction pipe leading from the reaction tank to the neutralization tank, sulfite or bisulfite is put into the neutralization tank. Thereby, manganese ions are turned into manganese dioxide and are made insoluble, and at the same time, excessive hypochlorite is reduced.

**[0073]** The quantity of the added alkaline agent is adjusted so that the pH value in the neutralization tank is 7 to 9.5. In this case, magnesium hydroxide does not deposit.

**[0074]** Also, sulfite or bisulfite is added so that the oxidation-reduction potential in the neutralization tank is 200 mV and higher, preferably 300 to 400 mV. If the oxidation-reduction potential is lower than this range, insolubilized manganese dioxide dissolves again. Further, undesirably, not only the consumption of chemicals increases, but also excessive sulfurous acid ions are detected as COD.

**[0075]** The liquid in the neutralization tank can be agitated by air. Thereby, excessive sulfurous acid ions are oxidized by the supplied air, and are turned into sulfate ions.

**[0076]** Further, if the oxidation-reduction potential is higher than this range, unreacted hypochlorite (residual chlorine) sometimes remains, and undesirably exerts an influence on a subsequent treatment process (for example, performance in removing heavy metals other than manganese, separation membrane used in the solid-liquid separation method, ion exchange resin for removing fluorine, and durability of activated charcoal for removing COD).

**[0077]** As sulfite or bisulfite, not only sodium sulfite, sodium bisulfite, or the like, but also combustion flue gas from which dust containing sulfur oxide has been removed can be used. However, sodium sulfite or sodium bisulfite is preferable.

**[0078]** Next, the reaction liquid of the neutralization tank is introduced into a solid-liquid separation tank. At this time, a heavy metal chelating agent is added in a pipe leading from the neutralization tank to the solid-liquid separation tank or in the solid-liquid separation tank. Thereby, heavy metals other than manganese can be deposited as solid content. If unreacted hypochlorite remains, the capability of removing heavy metals by using the heavy metal chelating agent is inhibited. Therefore, it is indispensable to remove excessive hypochlorite in the preceding neutralization tank.

**[0079]** As solid-liquid separation means, a membrane separation method can be used in addition to the conventional coagulative precipitation method. In the coagulative precipitation method, a high molecular coagulant is preferably added to the reaction liquid at the outlet of the neutralization tank (not shown) to facilitate the formation and precipitation of coagulated flocks. A supernatant liquid of the precipitation tank is discharged to the outside of the system as treated water, and precipitated solid substances including manganese dioxide and heavy metals are discharged as sludge.

**[0080]** When the membrane separation is used as the solid-liquid separation method, deterioration in membrane must sometimes be prevented. Therefore, unreacted hypochlorite is preferably removed in the preceding neutralization tank.

**[0081]** As a separation membrane, a tubular type or submerged type microfiltration (MF) membrane can be used.

**[0082]** When the membrane separation is used, membrane permeating liquid is discharged to the outside of the system as treated water, and solid substances including concentrated manganese dioxide and heavy metals are discharged as sludge.

**[0083]** The method shown in FIG. 2 can be applied to the case of desulfurization waste water in which heavy metals other than manganese, especially cadmium, coexist.

**[0084]** FIG. 3 shows still another example for carrying out a method in accordance with the first invention of the present invention.

**[0085]** In this method, hypochlorite is first added to waste water having been introduced into a reaction tank and the waste water is mixed. In this case as well, as in the methods shown in FIGS. 1 and 2, hypochlorite is added so that the oxidation-reduction potential in the reaction tank is 600 mV and higher, preferably 700 to 900 mV. Further, an alkaline agent is poured so that the pH value in the reaction tank is adjusted to 7 to 9.5. Thereby, manganese ions in the desulfurization waste water are turned into manganese dioxide and are deposited. As in the case shown in FIGS.

1 and 2, magnesium hydroxide does not deposit.

[0086] Next, the reaction liquid of the reaction tank is introduced into a neutralization tank. In the neutralization tank, sulfite or bisulfite is added so that the oxidation-reduction potential in the neutralization tank is 200 mV and higher, preferably 300 to 400 mV. If the oxidation-reduction potential is in this range, manganese dioxide does not turn into manganese ions by means of re-dissolution.

[0087] Further, the reaction liquid of the neutralization tank is introduced into a solid-liquid separation tank. At this time, a heavy metal chelating agent is added in a pipe leading from the neutralization tank to the solid-liquid separation tank or in the solid-liquid separation tank. Thereby, heavy metals other than manganese can be insolubilized as solid content.

[0088] When a submerged type microfiltration (MF) membrane separation method is used as a solid-liquid separation method, agitating air is supplied from under a separation membrane to produce a water flow in the solid-liquid separation tank in order to prevent the separation membrane from clogging. At this time, oxygen dissolves. When sulfite having been added in the preceding neutralization tank remains in a minute amount, therefore, sulfurous acid ions are favorably oxidized into sulfate ions. Membrane permeating liquid is discharged to the outside of the system as treated water, and solid substances including concentrated manganese dioxide and heavy metals are discharged as sludge.

[0089] The method shown in FIG. 3, like the method in FIG. 2, can be applied to the case of desulfurization waste water in which heavy metals other than manganese, especially cadmium, coexist.

[0090] According to the first invention of the present invention as described above, manganese ions and heavy metals in the desulfurization waste water can be removed easily and efficiently in a region ranging from neutrality to weak alkalinity.

[0091] Also, a low and steady concentration of manganese in treated water can be obtained. Since magnesium ions in the desulfurization waste water do not deposit as magnesium hydroxide, a smaller amount of sludge is produced.

#### Embodiments of second invention

[0092] Specific embodiments of an absorbent slurry treatment method and a flue gas desulfurization system in accordance with a second invention of the present invention will be described with reference to the accompanying drawings.

#### 1) Embodiment (No. 1)

[0093] FIG. 4 shows an example of a system capable of carrying out a method in accordance with the second invention of the present invention.

[0094] In FIG. 4, waste water containing heavy metals, which is discharged from a desulfurizer 1 is first sent to a mixing process (mixing tank 4). The principal ingredient of absorbent slurry 3a discharged from a desulfurization process (desulfurizer 1) is gypsum. The absorbent slurry 3a contains 20 to 30wt% of gypsum with respect to water, and in addition, contains heavy metals as a very minute amount of component. The weight percentage of heavy metals varies according to the components, properties and the like of fuel, so that it cannot be specified generally.

[0095] In this embodiment, after the desulfurization process, the mixing process in which a chelating agent is added, a gypsum separation process (solid content separation), a filtrate treatment process (oxidation process, membrane separation process), an activated charcoal adsorption process, and a fluorine adsorption process are carried out in this order.

#### (1) Mixing process

[0096] The mixing process is a process in which a chelating agent for collecting heavy metals, a coagulation assistant, and permanganate as necessary, are added to absorbent slurry to coagulate and deposit solid substances including heavy metals.

[0097] As the chelating agent for collecting heavy metals, high molecular heavy metal collectors of liquid having a chelate formation group such as dithiocarbamic acid group (-NH-CS<sub>2</sub>Na) and thiol group (-SNa) can be cited. The heavy metals in question are, although not subject to any special restriction, heavy metals such as Cd, Se and Hg. By adding the chelating agent for collecting heavy metals, microflocks having collected heavy metals are yielded.

[0098] The quantity of heavy metal chelating agent added in the mixing-process is determined appropriately according to the quantity of heavy metals in the absorbent and other factors. Usually, the heavy metal chelating agent of 5 mg/liter and more, preferably 10 to 30 mg/liter, is added to the absorbent slurry.

[0099] The coagulation assistant is a chemical that is added as necessary to make the flocks of collected heavy metal chelate large or to solidify unreacted heavy metal chelating agent. As the coagulation assistant, ferric chloride, ferric sulfate, or the like is used. Although the quantity of added coagulation assistant is not specified generally because

the necessity of adding coagulation assistant is determined by the components and properties of fuel, the coagulation assistant of 10 to 200 mg/liter, preferably 50 to 100 mg/liter, is usually added to the absorbent. This addition effects the formation of coarse flocks, resulting in improved separation property. The solid substances in mixed liquid, including these flocks, are separated by a gypsum separator 9 and are mixed in gypsum cake.

## (2) Gypsum separation process

[0100] The heavy metals coagulated before the removal of gypsum by the addition of the chelating agent and coagulation assistant in the above-described mixing process are mixed in gypsum cake and separated simultaneously with the gypsum separation. That is to say, the chelated heavy metals are separated and removed as impurities in gypsum.

[0101] In the present invention, since heavy metals etc. in filtrate 11 coming from the gypsum separation process have been removed, the treatment in the subsequent processes is easy even when some of the filtrate is extracted later as waste liquid.

[0102] Specifically, according to the present invention, the aforementioned heavy metal chelating agent or the like is added to the absorbent slurry drawn from the desulfurizer to effect gypsum separation. After all of the filtrate after gypsum separation is subjected to COD treatment, some of the filtrate is subjected to separation membrane treatment, and treated water is subjected to post-treatment such as activated charcoal treatment as waste water. Therefore, in the gypsum process, polluting substances such as heavy metals are removed and membrane separation liquid is extracted as waste water separately from concentrate, so that sludge is hardly produced in the post-treatment.

[0103] Also, some substances contained in the absorbent slurry change into a compound that is difficult to recover subsequently after an oxidizing agent has been added in the oxidation process. After heavy metals and the like are separated in gypsum by adding an chelating agent or the like before the gypsum separation as in the present invention, even if the filtrate undergoes the COD treatment (oxidation process), the compound that is difficult to recover and separate is prevented from being yielded, and it can be removed by the gypsum separation before the oxidation.

[0104] The gypsum obtained by the gypsum separator contains impurities such as heavy metals etc. turned into solid content, but the impurities have no problem concerning the purity of gypsum cake.

## (3) Filtrate treatment process

[0105] The filtrate treatment process in accordance with the present invention consists of an oxidation process and a membrane separation process, and a neutralization process is added to this filtrate treatment process as necessary.

[0106] In the present invention, heavy metals including manganese are removed by being mixed in gypsum in the gypsum separation process as described above, and then dehydration and filtration are effected. Since difficult-to-decompose COD components, fluorine, and the like are contained in the filtrate coming from the gypsum separator, these compounds in the filtrate 11 are treated.

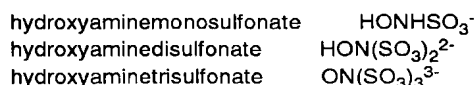
[0107] For example, the filtrate treatment process is carried out by a system in which an oxidation tank (oxidation reaction), a neutralization tank (neutralization reaction), and a separation membrane are arranged in succession.

[0108] In the oxidation tank (oxidation reaction) and the neutralization tank (neutralization reaction), hypochlorite is first added to decompose the difficult-to-decompose COD components (oxidation tank). Then, residual chlorine is reduced by a reducing agent (neutralization tank). Thereupon, slightly excessive reducing agent remains, so that the reducing agent is oxidized by air to provide a treated liquid with no problem.

## Oxidation process and neutralization process

[0109] In the oxidation process (COD decomposition process), an oxidizing agent is added to waste water to decompose nitrogen-sulfur compounds, which are COD components in waste water. Thereafter, in the neutralization process, the filtrate is adjusted from neutrality to weak alkalinity by alkali, and the reducing agent is further added as necessary, by which excessive oxidizing agent is decomposed and removed.

[0110] The filtrate 11 coming from the above-described gypsum separation process is sent to the oxidation process. This filtrate contains N-S compounds (inorganic COD components) mainly having the following composition yielded by the reaction of SO<sub>2</sub> with NO<sub>x</sub> in the desulfurizer and manganese ions.

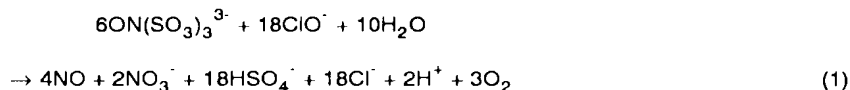


[0111] Acid 13a such as hydrochloric acid or sulfuric acid is added to the filtrate, and the pH value is adjusted to 4 and lower, preferably about 3 to 4 to save waste usage of chemicals. Thus, the quantity of added acid is determined

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appropriately so that the pH value is within this range. As the added acid 13a, hydrochloric acid is preferably used from the viewpoint of the prevention of scaling.

[0112] Subsequently, a predetermined amount of oxidizing agent such as hypochlorite is added based on the oxidation-reduction potential of waste water to decompose the difficult-to-decompose COD components (N-S compounds). As the oxidizing agent, hypochlorite, chlorine dioxide solution, or the like can be used. Of these compounds, sodium hypochlorite (NaOCl) is preferable from the viewpoints of treatment ability and economy. One example of reaction formula (1) at this time is given below.



[0113] The amount of added hypochlorite is usually about 2 to 8 moles, preferably about 3 to 5 moles, on a mole basis with respect to one mole of N-S compounds. In this reaction, the temperature is preferably 40°C and higher, and the residence time is preferably 2 hours and longer. Also, in this process, manganese ions (bivalent) contained in the filtrate 11 coming from the gypsum separation process are not oxidized and are still kept in a dissolved state.

[0114] In the neutralization process, the pH value of the filtrate containing the oxidizing agent added in the oxidation process is first adjusted to 7 to 8. At this time, manganese ions (bivalent) is oxidized and deposited as manganese dioxide (quadrivalent).

[0115] Further, in order to treat the residual chlorine, a reducing agent is added to effect neutralization. After the N-S compounds are decomposed, it is preferable that any reducing agent of sodium sulfite ( $\text{Na}_2\text{SO}_3$ ), sodium hydrogen-sulfite ( $\text{NaHSO}_3$ ), sodium thiosulfate ( $\text{Na}_2\text{S}_2\text{O}_3$ ), and the like with an equivalent almost equal to that of the residual oxidizing agent detected by the oxidation-reduction potential of waste water be added to decompose excessive oxidizing agent such as sodium hypochlorite.

[0116] Also, as an alkali added in the neutralization process, for example, sodium hydroxide or potassium hydroxide can be used.

### Membrane separation process

[0117] For the liquid having undergone the treatment in the above-described oxidation process and neutralization process, most of the treated liquid is returned to the desulfurization process as concentrate 25 to be reused. Specifically, at the final stage of the filtrate treatment process, SS components are first removed by membrane separation, and the removed SS components are returned again to the desulfurization process as the concentrate 25. The concentrate returned from a membrane separation tank to the desulfurizer through a concentration pump is about 70wt% of the filtrate 11 coming from the gypsum separation process.

[0118] On the other hand, a necessary amount of membrane filtrate 28a separated in the membrane separation process is sent to the subsequent waste water treatment process. In the waste water treatment, activated charcoal adsorption is effected in an activated charcoal adsorption tower 34 to treat organic COD components contained in the membrane filtrate 28a, and then fluorine adsorption treatment using a fluorine adsorption resin is effected in a fluorine adsorption tower 38. Thereby, the filtrate is discharged as purified treated water.

[0119] As a separation membrane 21, for example, a tubular type microfiltration membrane, a submerged type flat-plate microfiltration membrane, and a submerged type hollow-fiber microfiltration membrane can be cited, and any type of membrane can be used. For example, in the case of the submerged type hollow-fiber microfiltration membrane, if slightly decompressed filtrate is caused to pass through a hollow tube in the membrane, solid content adheres to the surface, and only water content flows inside and is separated. The separation membranes are arranged at the slightly upper part in the vicinity of the center of a membrane separation tank 20. If the separation membrane is contaminated, it is washed appropriately. The separation membrane is in a state such as to be always vibrated by the liquid flow caused by air blown from an air-diffusing pipe located under the separation membrane. The quantity of air is usually in the range of 0.1 to 0.4 m<sup>3</sup>/h per one air-diffusing pipe.

[0120] The adhesion of solid content to the membrane surface is prevented by the vibration of membrane caused by bubbling. Some of the solid content floats and the remainder precipitates at the bottom of the membrane separation tank 20. The precipitate can be returned to the mixing tank 4 before the gypsum separation as necessary by a precipitate pump 26. This precipitate contains deposited manganese dioxide, which is mixed in gypsum and separated simultaneously with the gypsum separation.

[0121] The reason for separating filtrate by the separation membrane is that solid content is prevented from being sent to the waste water treatment process, and therefore solid content is removed by the solid-liquid separation. In the

present invention, the solid-liquid separation is effected by using the separation membrane, so that a filtration process (sand filtration etc.) need not be provided before the activated charcoal adsorption tower.

#### (4) Activated charcoal adsorption process

**[0122]** The activated charcoal adsorption process is a process in which the membrane filtrate 28a having undergone the membrane separation process is brought into contact with activated charcoal as waste water to remove organic COD components by means of adsorption.

**[0123]** After being stored in a membrane filtrate tank 32, the membrane filtrate 28a is introduced into the activated charcoal adsorption tank 34 by using a pump 33. The membrane filtrate 28a is caused to pass through a granulated activated charcoal layer in the activated charcoal adsorption tower 34, by which organic COD components mainly caused by industrial water are removed by means of adsorption.

**[0124]** The waste water from which organic COD components have been removed is introduced to the fluorine adsorption process and is treated. The activated charcoal having been clogged with impurities after water has been caused to pass through for a certain period of time is back washed by water, by which the impurities can be removed.

#### (5) Fluorine adsorption process

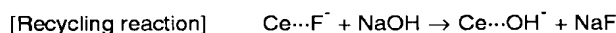
**[0125]** The fluorine adsorption process is a process in which the waste water having been treated in the activated charcoal adsorption process is brought into contact with a fluorine adsorption resin to remove the remaining fluorine by means of adsorption, and thereafter the pH value of the waste water is adjusted by an alkaline agent.

**[0126]** In the fluorine adsorption process, after the pH value of waste water is adjusted to about 2 to 4 by using mineral acid such as hydrochloric acid, the waste water whose pH value has been adjusted is caused to pass through a fluorine adsorption resin layer in the fluorine adsorption tower, by which minute amounts of fluorine ions remaining in the liquid are removed by means of adsorption. For the fluorine adsorption resin, various types are available in terms of functional group and carrier metal. Concretely, phosphomethylamino group chelate resin, zirconium carrier type resin, cesium carrier type resin, and the like are cited. Of these resins, zirconium carrier type resin and cesium carrier type resin are preferably used.

**[0127]** Of these resins, for example, the cesium carrier type resin reacts with fluorine ion as described below.



**[0128]** The adsorption resin whose fluorine adsorbing capability has decreased after water has been caused to pass through for a certain period of time is recycled by the reaction with an alkaline agent such as sodium hydroxide as described below, and thereafter is washed by mineral acid such as hydrochloric acid and water, whereby the adsorption resin can be recycled.



**[0129]** Recycled waste liquid 42 discharged at this time can be returned from a recycled waste liquid tank 43 to the desulfurizer 1. In this case, fluorine ions in the recycled waste liquid are collected by large amounts of calcium ions in the desulfurizer. The fluorine ions are fixed as calcium fluoride, and are discharged by being contained in the yielded gypsum ( $\text{CaSO}_4$ ). In particular, this recycled waste liquid 42 contains excessive NaOH, which gives a favorable influence to the desulfurization performance of the desulfurizer.

**[0130]** On the other hand, for fluorine treated water 39 from which fluorine ions have been removed by means of adsorption, the pH value is adjusted to about 6 to 8 by using an alkaline agent such as sodium hydroxide. Thereafter, the fluorine treated water 39 is discharged or recycled.

#### 2) Embodiment (No. 2)

**[0131]** FIG. 5 shows one embodiment of a system using a method in accordance with the second invention of the present invention.

**[0132]** In this embodiment, a fixing substance such as permanganate 7 is also added to the absorbent slurry in the mixing tank 4. Usually, manganese and the like are present in the absorbent liquid, and for example, manganese is a substance subject to regulation. Therefore, the absorbent liquid cannot be discharged without treatment.

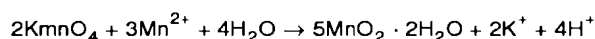
**[0133]** Conventionally, therefore, there has been used a method in which the absorbent slurry is sedimented in a

form of hydroxide by increasing the pH value to 10 and higher, by which the absorbent slurry is separated. In this method, however, magnesium contained in the desulfurization waste water is also deposited undesirably as magnesium hydroxide. Therefore, to prevent the coprecipitation of magnesium, manganese is preferably separated and removed after being changed into a form of manganese dioxide in removing manganese ions. For this purpose, permanganate is added.

[0134] By adding permanganate 7 in the mixing tank 4 as described above, manganese in the absorbent slurry is separated into gypsum and removed in the gypsum separation process.

[0135] Generally, manganese has a smaller affinity force with a heavy metal chelating agent than other heavy metals, so that other heavy metals deposit earlier as solid content. Therefore, in some cases, it is difficult to remove manganese by a heavy metal chelating agent only. For this reason, for manganese ions (bivalent) with a low efficiency of removal using a chelating agent (capability in changing into solid content), it is effective to add a particular fixing substance (for example, permanganate). In this case, it is preferable to add permanganate in the vicinity of almost neutral pH value. As permanganate, potassium permanganate, for example, can be cited.

[0136] When permanganate is used as described above, permanganate is added so that the quantity thereof is usually 1 to 5 times, preferably 1.5 to 3 times, the quantity of manganese ions (bivalent) in the absorbent slurry by weight ratio. The reaction when permanganate is added takes place as expressed by the following reaction formula.



### 3) Embodiment (No. 3)

[0137] In this embodiment, the above-described membrane separation tank is provided in an absorption tower of the desulfurizer 1 in a wet lime-gypsum process flue gas desulfurization system in which sulfur oxide gas is absorbed and separated by using absorbent slurry. Also, when the neutralization tank in which a reducing agent is added to treated liquid coming from the oxidation tank is provided between the oxidation tank and the membrane separation tank, the neutralization tank is also provided in the absorption tower of the desulfurizer 1 in addition to the membrane separation tank.

[0138] FIG. 6 shows the outline of a system in accordance with this embodiment, and FIG. 7 shows the outline of a system of a mode in which a fixing substance such as permanganate is further added.

[0139] The system in accordance with this embodiment is an integral type system of the filtrate treatment process and the desulfurizer 1, and the filtrate treatment process is incorporated in the desulfurizer. Therefore, this system is efficient because even if the concentrate 25 obtained by the membrane separation is not returned to the desulfurizer 1 through the pump, the concentrate 25 is gathered in an absorbent tank 1a in the desulfurizer as it is.

[0140] According to the second invention of the present invention as described above, in the treatment of absorbent in the flue gas desulfurization system, the treatment efficiency in the desulfurization process and waste water treatment process can be enhanced, and the quantity of sludge discharged by the treatment can be decreased.

[0141] Specifically, in the present invention, by effectively combining and integrating the desulfurization process (desulfurizer) with the absorbent slurry treatment process (gypsum separation), the quantity of wastes in the whole system can be decreased, and the burden on the post-treatment process can be alleviated.

[0142] Also, according to the present invention, components of difficult-to-decompose COD components, heavy metals, fluorine, and the like can be removed efficiently and sufficiently from the absorbent slurry of the wet type flue gas desulfurization system for coal burning flue gas, and also sludge can be prevented from being produced in the waste water treatment. Therefore, an efficient operation of the desulfurizer and treatment of waste water can be made easy.

[0143] Further, the resin recycled waste liquid in the fluorine treatment process for waste water treatment contains excessive NaOH with a high pH value. Therefore, by returning the recycled waste water to the desulfurizer, a favorable influence is given to the desulfurization performance of the desulfurizer.

[0144] Thus, according to the second invention of the present invention, the desulfurization waste water treatment process can be simplified, and also the quantity of deposited sludge is far smaller than the quantity of by-product gypsum, and sludge is hardly produced. Also, since no hydroxide is produced in the waste water treatment, the hydroxide need not be mixed with gypsum, so that the water content and purity of gypsum are not influenced adversely.

[0145] Further, by using the separation process using the separation membrane in place of the conventional coagulative separation process, sand filtration process, and the like, the treatment process can be simplified, and also the increased size of equipment and the necessity of a large-scale treatment facility can be avoided.

Embodiments of third invention

## 1) Embodiment (No. 4)

**[0146]** FIG. 8 shows an example of a system capable of carrying out a method in accordance with a third invention of the present invention.

**[0147]** In FIG. 8, some of absorbent slurry containing heavy metals, which is discharged from an absorption tower 102, a part of a desulfurizer, is first extracted and sent to a gypsum separator 108. The principal ingredient of the absorbent slurry discharged from the desulfurization process is gypsum, the absorbent slurry containing 20 to 30wt% of gypsum with respect to water. In addition, the absorbent slurry contains heavy metals as a very minute amount of component. The weight percentage of heavy metals varies according to the components, properties and the like of fuel, so that it cannot be specified generally.

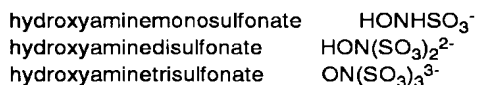
**[0148]** In this embodiment, after gypsum separation (solid content separation) is effected, the filtrate is treated in an oxidation process, a neutralization process (neutralization reaction), and a solid-liquid separation process in this order. This filtrate treatment process is carried out by a treatment system equipped with an oxidation tank 111, a neutralization tank 116, and a membrane separation tank 117 as shown in FIG. 8, for example.

**[0149]** In the present invention, the absorbent slurry containing heavy metals such as manganese as described above is first dehydrated and filtrated in the gypsum separation process. The filtrate coming from a gypsum separator contains heavy metals such as manganese, difficult-to-decompose COD components, and the like, so that these compounds in the filtrate 110 is treated.

**[0150]** Specifically, after the gypsum separation, an oxidizing agent such as hypochlorite is added to the filtrate in the oxidation tank, and then the pH value of the filtrate is adjusted to 7 to 9.5 in the neutralization tank. The filtrate whose pH value has been adjusted is subjected to solid-liquid separation by membrane separation or the like, by which heavy metals such as manganese contained in the filtrate are removed.

## (i) Oxidation process

**[0151]** The filtrate 110 coming from the above-described gypsum separation process is sent to the oxidation process. This filtrate contains N-S compounds (inorganic COD components) mainly having the following composition yielded by the reaction of  $\text{SO}_2$  with  $\text{NO}_x$  in the desulfurizer.



**[0152]** Acid 112 such as hydrochloric acid or sulfuric acid is added to the filtrate so that the pH value is adjusted to 3 to 4 to save wasteful usage of chemicals. Thus, the quantity of added acid is determined appropriately so that the pH value is within this range. As the added acid 112, hydrochloric acid is preferably used from the viewpoint of the prevention of scaling.

**[0153]** Subsequently, in the oxidation tank 111, an oxidizing agent such as hypochlorite is added to decompose difficult-to-decompose COD components. As hypochlorite, sodium hypochlorite, bleaching powder, and the like can be used, and sodium hypochlorite ( $\text{NaOCl}$ ) is preferably used from the viewpoint of handling.

**[0154]** At this time, it is preferable that the content of difficult-to-decompose COD components (N-S compounds) be determined based on the oxidation-reduction potential (ORP) of waste water, and an oxidizing agent of a predetermined amount corresponding the above content be added to decompose the N-S compounds. The reaction taking place when sodium hypochlorite is used as the oxidizing agent is expressed by the above-described reaction formula (1).

**[0155]** The quantity of added hypochlorite is usually about 2 to 8 moles, preferably about 3 to 5 moles, on a mole basis with respect to one mole of N-S compound. In this reaction, the temperature is preferably 40°C and higher, and the residence time is preferably 2 hours and longer.

**[0156]** On the other hand, the pH value of desulfurization waste water is usually in an acidic region, and in the case where an oxidizable substance such as an organic substance is present in the waste water, when the waste water is mixed with hypochlorite, hypochlorite is consumed by the oxidation.

**[0157]** Therefore, in the oxidation process in the present invention, as a necessity for oxidation of oxidizable substance and manganese ions, hypochlorite is added so that the oxidation-reduction potential in the oxidation tank is 600 mV and higher, preferably 700 to 900 mV. If the oxidation-reduction potential is lower than this range, the oxidation of manganese ions is insufficient, and if it is higher than this range, the addition of hypochlorite becomes excessive, so that the consumption of chemicals increases undesirably.

## (ii) Neutralization process

**[0158]** Next, the reaction liquid of the oxidation tank 111 is introduced into the neutralization tank 116. In the neutralization tank 116, an alkaline agent 114 is added so that the pH value is 7 to 9.5. As the alkaline agent, sodium hydroxide, calcium hydroxide, potassium hydroxide, or the like can be used. Of these compounds, calcium hydroxide increases the quantity of sludge, and potassium hydroxide is expensive, causing a poor economy. Therefore, considering economical efficiency and convenience in handling, sodium hydroxide is especially preferable.

**[0159]** In the neutralization tank 116, manganese ions are turned into manganese dioxide by the alkaline agent, and the manganese dioxide deposits as a soluble solid content. However, since the pH value is adjusted to 7 to 9.5, magnesium hydroxide does not deposit.

**[0160]** Also, in some cases, unreacted hypochlorite remains in the reaction liquid of the oxidation tank. Therefore, a reducing agent 115 such as sulfite, sulfurous acid gas, or bisulfite is preferably added to remove residual chlorine.

**[0161]** Specifically, if the oxidation-reduction potential of waste water is not 200 mV and higher, preferably 300 to 400 mV, after the decomposition of N-S compounds, a reducing agent is added so that the oxidation-reduction potential is in this range, by which excessive oxidizing agent such as hypochlorite is decomposed. If the oxidation-reduction potential is lower than this range, insolubilized manganese dioxide dissolves again easily. Further, undesirably, not only the consumption of chemicals increases, but also excessive reducing agent is detected as COD. As sulfite or bisulfite, not only sodium sulfite ( $\text{Na}_2\text{SO}_3$ ), sodium bisulfite ( $\text{NaHSO}_3$ ), sodium thiosulfate ( $\text{Na}_2\text{S}_2\text{O}_3$ ), or the like, but also combustion flue gas from which dust containing sulfur oxide has been removed can be used.

## (iii) Solid-liquid separation process

**[0162]** Next, the reaction liquid of the neutralization tank 116 is introduced into the membrane separation tank 117. The solid-liquid separation method is not subject to any special restriction. For example, the membrane separation method or the coagulative precipitation method can be used, and the membrane separation method is preferably used. In the case of the coagulative precipitation method, a high molecular coagulant is preferably added to the reaction liquid at the outlet of the neutralization tank 116 to facilitate the formation and precipitation of coagulated flocks.

**[0163]** FIG. 8 shows an embodiment in which the membrane separation method is used by the use of the membrane separation tank 117.

**[0164]** Some of the liquid having undergone the treatment in the above-described oxidation process and neutralization process is returned to the preceding stage of the gypsum separator 108 as concentrate 123. The concentrate 123 returned from the membrane separation tank 117 to the preceding stage of the gypsum separator 108 through a concentrate pump 122 usually has a weight percentage of about 0.5 to 1wt% of the filtrate of the membrane separation tank. This precipitate contains deposited manganese dioxide, and is mixed in gypsum and separated simultaneously with the gypsum separation. Also, overflow water 124 coming from the membrane separation tank 117 is sent again to the absorption tower 102 through a limestone preparation tank 125.

**[0165]** On the other hand, a necessary amount of membrane filtrate separated in the membrane separation process is sent to the subsequent waste water treatment process. In the waste water treatment, for example, activated charcoal adsorption is effected in an activated charcoal adsorption tower to treat organic COD components contained in the membrane filtrate 121, and then fluorine adsorption treatment using a fluorine adsorption resin is effected as necessary. Thereby, the filtrate is discharged as purified treated water.

**[0166]** As a separation membrane 118, for example, a tubular type microfiltration membrane, a submerged type flat-plate microfiltration membrane, and a submerged type hollow-fiber microfiltration membrane can be cited, and any type of membrane can be used. For example, in the case of the submerged type hollow-fiber microfiltration membrane, if slightly decompressed filtrate is caused to pass through a hollow tube in the membrane, solid content adheres to the surface, and only water content flows inside and is separated. The separation membranes are arranged at the slightly upper part in the vicinity of the center of a membrane separation tank 117. If the separation membrane is contaminated, it is washed appropriately. The separation membrane is in a state such as to be always vibrated by the liquid flow caused by air blown from an air-diffusing pipe located under the separation membrane. The quantity of air is usually in the range of 0.1 to 0.4  $\text{m}^3/\text{h}$  per one air-diffusing pipe. Thereby, the adhesion of solid content to the membrane surface is prevented. Also, when sulfite having been added in the preceding neutralization tank remains in a minute amount, sulfurous acid ions are favorably oxidized into sulfate ions by the air agitation.

**[0167]** Some of the solid content yielded by membrane filtration floats and the remainder precipitates at the bottom of the membrane separation tank 117. The precipitate can be returned to the preceding stage of the gypsum separator 108 through the concentrate pump 122 as the solid substance concentrate 123 as described above.

**[0168]** The reason for separating filtrate by the separation membrane 118 is that solid content is prevented from being sent to the waste water treatment process, and therefore solid content is removed by the solid-liquid separation. In the present invention, the solid-liquid separation is effected by using the separation membrane, so that a filtration

process (sand filtration etc.) need not be provided before the activated charcoal adsorption tower.

2) Embodiment (No. 5)

**[0169]** FIG. 9 shows an example of another system for carrying out the third invention of the present invention.

**[0170]** In the system shown in FIG. 9, some of absorbent slurry containing heavy metals, which is discharged from the absorption tower 102, a part of the desulfurizer, is extracted and sent to the gypsum separator 108 as in the case of the above-described embodiment (No. 4). In this embodiment, of the filtrate 110 having undergone the gypsum separation (solid-liquid separation), some filtrate 110b is treated in the oxidation process, the neutralization process (neutralization reaction), and the solid-liquid separation process in this order. This treatment process of the filtrate 110b is carried out by a treatment system equipped with the oxidation tank 111, the neutralization tank 116, and the membrane separation tank 117 as shown in FIG. 9.

**[0171]** The filtrate 110b can be treated in the oxidation process, the neutralization process, and the solid-liquid separation process, which are the same as those in the above-described embodiment (No. 4). Specifically, after an oxidizing agent such as hypochlorite is added to the filtrate 110b in the oxidation tank, the pH value of the filtrate is adjusted to 7 to 9.5 in the neutralization tank. The filtrate whose pH value has been adjusted is subjected to solid-liquid separation by membrane separation or the like. Thereby, heavy metals such as manganese contained in the filtrate 110b are removed, and also difficult-to-decompose COD components are decomposed and removed.

**[0172]** On the other hand, other filtrate 110a is introduced into the limestone preparation tank 125, and then is returned to the absorption tower 102. Therefore, in this embodiment, overflow water is not taken out of the membrane separation tank 117 to be introduced into the tank 125. Solid substance concentrate 123a is introduced from the membrane separation tank 117 to the preceding stage of the gypsum separator 108, and the membrane filtrate 121 is discharged to waste water treatment.

3) Embodiment (No. 6)

**[0173]** FIGS. 10 and 11 show an example of still another system for carrying out the third invention of the present invention.

**[0174]** In the system of this embodiment, some of absorbent slurry discharged from the absorption tower 102, a part of the desulfurizer, is extracted and sent to the gypsum separator 108. In this embodiment, there is provided a mixing tank 130 in which a heavy metal chelating agent 131 or the like is added to and mixed with the absorbent slurry. After undergoing this mixing process, the absorbent slurry is sent to the gypsum separator 108.

**[0175]** Specifically, the waste water containing heavy metals, which is discharged from the absorption tower 102, is first sent to the mixing tank 130. The principal ingredient of absorbent slurry discharged from the desulfurization process (desulfurizer) is gypsum, the absorbent slurry containing 20 to 30wt% of gypsum with respect to water. In addition, the absorbent slurry contains heavy metals as a very minute amount of component. The weight percentage of heavy metals in waste water varies according to the components, properties and the like of fuel, so that it cannot be specified generally.

**[0176]** In this embodiment, to remove such heavy metals from the waste water, after undergoing the mixing process, the absorbent slurry is treated in the gypsum separation process, the oxidation process, the neutralization process, and the membrane separation process in this order.

**[0177]** The above-described mixing process is a process in which a chelating agent for collecting heavy metals, a coagulation assistant, and permanganate as necessary, are added to absorbent slurry to coagulate and deposit solid substances including heavy metals.

**[0178]** As the chelating agent for collecting heavy metals, high molecular heavy metal collectors of liquid having a chelate formation group such as dithiocarbamic acid group (-NH-CS<sub>2</sub>Na) and thiol group (-SNa) can be cited. The heavy metals in question are, although not subject to any special restriction, heavy metals such as Cd, Se and Hg. By usually adding 10 to 100 mg/L of chelating agent for collecting heavy metals, microflocks having collected heavy metals are yielded.

**[0179]** The quantity of heavy metal chelating agent added in this process is determined appropriately according to the quantity of heavy metals in the absorbent and other factors. Usually, the heavy metal chelating agent of 5 mg/liter and more, preferably 10 to 30 mg/liter, is added to the absorbent slurry.

**[0180]** The coagulation assistant is a chemical that is added as necessary to make the flocks of collected heavy metal chelate large or to solidify unreacted heavy metal chelating agent. As the coagulation assistant, ferric chloride, ferric sulfate, or the like is used. Although the quantity of added coagulation assistant is not specified generally because the necessity of adding coagulation assistant is determined by the components and properties of fuel, the coagulation assistant of 10 to 200 mg/liter, preferably 50 to 100 mg/liter, is usually added to the absorbent. This addition effects the formation of coarse flocks, resulting in improved separation property. The solid substances in mixed liquid, including

these flocks, are separated by the gypsum separator 108 and are mixed in gypsum cake 109.

[0181] In this embodiment, after the gypsum separator 108 in which gypsum is separated, there are provided the oxidation tank 111 (oxidation process) in which the pH value of all or some of filtrate from which gypsum has been separated is adjusted to 3 to 4 and an oxidizing agent is added, the neutralization tank 116 (neutralization process) in which an alkaline agent is mixed in the liquid coming from the oxidation tank to adjust the pH value to 7 to 9.5, and the membrane separation tank 117 (solid-liquid separation process) in which the liquid coming from the neutralization tank is subjected to solid-liquid separation by using a membrane. These oxidation tank, neutralization tank, and membrane separation tank are arranged vertically as a unit under the gypsum separator so that the liquid flows down naturally from the gypsum separator to the oxidation tank, from the oxidation tank to the neutralization tank, and from the neutralization tank to the membrane separation tank in succession.

[0182] FIG. 10 shows a mode in which all of the filtrate from which gypsum has been separated is charged into the oxidation tank 111, and FIG. 11 shows a mode in which some of the filtrate from which gypsum has been separated is charged into the oxidation tank 111.

[0183] The filtrate 110, 110b charged into the oxidation tank 111 is treated in the oxidation process, neutralization process, and solid-liquid separation process as in the case of the above-described embodiment (No. 4). Specifically, after an oxidizing agent such as hypochlorite is added to the filtrate in the oxidation tank, the pH value of the filtrate is adjusted to 7 to 9.5 in the neutralization tank 116. The liquid whose pH value has been adjusted is subjected to solid-liquid separation by membrane separation or the like. Thereby, heavy metals such as manganese contained in the filtrate 110, 110b are removed, and also difficult-to-decompose COD components are decomposed and separated.

[0184] In the system shown in FIG. 10, overflow water is taken out of the membrane separation tank 117 and is introduced into the limestone preparation tank 125. Solid substance concentrate 123b is introduced from the membrane separation tank 117 to the mixing tank 130 at the preceding stage of the gypsum separator 108, and the membrane filtrate 121 is discharged to the waste water treatment.

[0185] On the other hand, the filtrate 110a in the system shown in FIG. 11 is introduced into the limestone preparation tank 125, and then is returned to the absorption tower 102. In the mode shown in FIG. 11, overflow water is not taken out of the membrane separation tank 117 to be introduced into the tank 125.

[0186] According to this embodiment, since the oxidation tank 111, the neutralization tank 116, and the membrane separation tank 117 are arranged vertically on the downstream side of the gypsum separator 108, the installation area of the unit is small, and the whole system is made compact. Also, the system can be operated efficiently because the liquid flows down naturally.

#### 4) Embodiment (No. 7)

[0187] FIGS. 12 and 13 show an example of still another system for carrying out the third invention of the present invention.

[0188] In the system of this embodiment, as in the case of the above-described embodiment (No. 6), there is provided the mixing tank 130 in which a heavy metal chelating agent 131 or the like is added to and mixed with the absorbent slurry. After undergoing this mixing process, the absorbent slurry is sent to the gypsum separator 108. After undergoing the gypsum separation process, the absorbent slurry is treated in the oxidation process, the neutralization process, and the membrane separation process in this order.

[0189] In this embodiment, after the gypsum separator 108, there are provided the oxidation tank 111 in which the pH value of all or some of filtrate from which gypsum has been separated is adjusted to 3 to 4 and an oxidizing agent is added, the neutralization tank 116 in which an alkaline agent is mixed in the liquid coming from the oxidation tank to adjust the pH value to 7 to 9.5, and the membrane separation tank 117 in which the liquid coming from the neutralization tank is subjected to solid-liquid separation by using a membrane. These oxidation tank, neutralization tank, and membrane separation tank are arranged vertically under the gypsum separator so that the liquid flows down naturally from the gypsum separator to the oxidation tank and from the neutralization tank adjacent to the oxidation tank to the membrane separation tank in succession.

[0190] FIG. 12 shows a mode in which all of the filtrate from which gypsum has been separated is charged into the oxidation tank 111, and FIG. 13 shows a mode in which some of the filtrate from which gypsum has been separated is charged into the oxidation tank 111. The process in each tank is the same as that in the above-described embodiment (No. 6).

[0191] In the system shown in FIG. 12, overflow water is taken out of the membrane separation tank 117 and is introduced into the limestone preparation tank 125. On the other hand, the solid substance concentrate 123 is introduced into the mixing tank 130 at the preceding stage of the gypsum separator 108, and the membrane filtrate 121 is discharged to the waste water treatment. Also, the filtrate 110a in the system shown in FIG. 13 is introduced into the limestone preparation tank 125, and then is returned to the absorption tower 102. In the mode shown in FIG. 13, overflow water is not taken out of the membrane separation tank 117 to be introduced into the tank 125.

[0192] According to this embodiment, like the above-described embodiment (No. 6), since the oxidation tank 111 and the membrane separation tank 117 are arranged vertically on the downstream side of the gypsum separator 108, the installation area of the unit is small, and the whole system is made compact. Also, the system can be operated efficiently because the liquid flows down naturally.

[0193] As described above, according to the third invention of the present invention, by removing N-S compounds having an influence on the desulfurization performance, an adverse influence on the desulfurization performance of the flue gas desulfurization system can be avoided. Also, since the quantity of deposited sludge is far smaller than the quantity of by-product gypsum, and sludge is hardly produced, even if solid substance concentrate is sent again to the preceding stage of the gypsum separator, the water content and purity of gypsum are not influenced adversely.

[0194] Also, when sodium hypochlorite or the like is used as an oxidizing agent, because it is an inexpensive chemical, the running cost is low.

[0195] Further, both of N-S compounds, which are difficult-to-decompose COD components, and manganese ions  $Mn^{2+}$  can be treated efficiently at the same time, and the burden on the waste water treatment can be alleviated, so that the waste water treatment system can be simplified. According to the present invention as described above, waste water containing heavy metals, especially manganese, discharged from the wet type flue gas desulfurizer can be treated, so that the concentration of manganese in the treated water is low and stable.

[0196] The present invention will be described below in detail with reference to working examples. The present invention is not restricted by these working examples.

#### Working Example

##### Working example 1

[0197] As waste water discharged from a desulfurizer for boiler combustion flue gas, desulfurization waste water having water quality given in Table 1 below was treated by the flow shown in FIG. 1 under the treatment conditions given in Table 2. The quality of treated water and the quantity of produced sludge in this treatment are given in Table 2.

[0198] From Table 2, it can be seen that if the quantity of added chlorine was 50 mg/L and larger, the quantity of manganese ions  $Mn^{2+}$  in the treated water was 10 mg/L and smaller.

Table 1

pH	5.9
$Mn^{2+}$	40mg/L
$Cd^{2+}$	0.5mg/L
$SO_3^{2-}$	< 5mg/L
ORP	320mV

Table 2

Reaction tank	Added chlorine (mg/L)	20	50	100
	ORP (mV)	450	600	780
Neutralization tank	pH(-)	8	8	8
	ORP (mV)	430	580	750
	Residual chlorine (mg/L)	>0.05	12	17
Treated water	$Mn^{2+}$ (mg/L)	30	8	>1
Quantity of sludge (mg/L):SS		10	45	60

##### Comparative example 1

[0199] The pH value of the desulfurization waste water having the water quality given in Table 1 was adjusted to 11 by sodium hydroxide, and a supernatant liquid filtrated by a filter paper was made treated water. For this treated water, the quantity of manganese ions in the treated water was 3.8 mg/L, and the quantity of sludge produced in this treatment was about 12,000 mg/L.

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### Working example 2

[0200] As in the case of working example 1, desulfurization waste water having water quality given in Table 1 was treated by the flow shown in FIG. 2 under the treatment conditions given in Table 3. The quality of treated water and the quantity of produced sludge in this treatment are given in Table 3.

[0201] From Table 3, it can be seen that the quantity of manganese ions in the treated water was 1 mg/L and smaller, but if residual chlorine was present in the neutralization tank, cadmium was not removed at all, and under a treatment condition that residual chlorine was absent or sulfurous acid ions were excessive, cadmium was removed.

Table 3

Reaction tank	Added chlorine (mg/L)	100	100	100
	ORP (mV)	780	780	780
Neutralization tank	pH(-)	8	8	8
	Added bisulfite (mg/L)	0	50	100
	ORP (mV)	750	350	200
	Residual chlorine (mg/L)	17	<0.05	<0.05
	Residual $\text{SO}_3^{2-}$ (mg/L)	-	<1	<1
Added heavy metal chelating agent (mg/L)		30	30	30
Treated water	$\text{Mn}^{2+}$ (mg/L)	<1	<1	<1
	$\text{Cd}^{2+}$ (Mg/L)	0.5	<0.1	<0.1
Quantity of sludge (mg/L)		65	65	65

### Working example 3

[0202] As in the case of working example 1, desulfurization waste water having water quality given in Table 1 was treated by the flow shown in FIG. 2 under the treatment conditions given in Table 4. The quality of treated water and the quantity of produced sludge in this treatment are given in Table 4.

Table 4

Reaction tank	Added chlorine (mg/L)	100	100	100
	ORP (mV)	750	750	750
	pH(-)	9	9	9
Neutralization tank	Added bisulfite (mg/L)	0	50	100
	ORP (mV)	750	350	170
	Residual chlorine (mg/L)	17	<0.05	<0.05
	Residual $\text{SO}_3^{2-}$ (mg/L)	-	< 1	7
Added heavy metal chelating agent (mg/L)		30	30	30
Treated water	$\text{Mn}^{2+}$ (mg/L)	<1	<1	1.6
	$\text{Cd}^{2+}$ (Mg/L)	0.5	<0.1	<0.1
Quantity of sludge (mg/L)		70	70	70

[0203] From Table 4, it can be seen that when residual chlorine was present in the neutralization tank (ORP 750 mV), the quantity of manganese ions in the treated water was 1 mg/L and smaller, but cadmium was not removed at all. When residual chlorine and sulfurous acid ions were not present (ORP 350 mV), the quantity of manganese ions in the treated water was 1 mg/L, and the quantity of cadmium was 0.1 mg/L. When sulfurous acid ions are excessive (ORP 170 mV), cadmium was removed to 0.1 mg/L. The quantity of manganese ions was 1.6 mg/L, but the treated water regulation value of 10 mg/L could be attained.

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## Working examples 4 and 5 and comparative example 2

[0204] In these working examples, flue gas of 200 m<sup>3</sup>N/h taken out of a small-sized pulverized coal firing boiler (not shown) was treated by using the flue gas desulfurization systems shown in FIGS. 8 and 10 (working example 4) and in FIGS. 9 and 11 (working example 5) after dust removal. Also, in comparative example 2, the addition of sodium hypochlorite was stopped in working example 4 in which the treatment system shown in FIGS. 8 and 10 was used.

[0205] Table 5 gives the properties of flue gas and slurry in the above-described flue gas treatment and measurement results in each tank.

Table 5

		Working example 4			Working example 5			Comparative example 2
Treated flue gas concentration (ppm)	SO <sub>2</sub>	3000			3000			3000
Treated flue gas concentration (ppm)	NO <sub>x</sub>	1000			1000			1000
Outlet ga (ppm)	SO <sub>2</sub> concentration	120			120			120
Absorbent slurry	pH (-)	5.6			5.6			5.1
Absorbent slurry	SO <sub>3</sub> <sup>2-</sup> (mmol/l)	<1			<1			4
Absorbent slurry (mmol/l)	NS Compound	Non-detected			Non-detected			25
Absorbent slurry	Mn <sup>2+</sup> (ppm)	20			40			40
Oxidation tan	pH (-)	3.5			3.5			5.1
Addition ratio of sodium hypochlorite (mol/l)		0.15			0.15			0
Neutralization tank	pH (-)	6	7	8	6	7	8	5.1
Neutralization tank	ORP (mV)	650	500	440	670	510	430	-
Membrane filtrate	Mn (ppm)	15	5	< 1	20	8	< 1	40
Membrane filtrate	ClO <sup>-</sup> (ppm)	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	40
Membrane filtrate	SO <sub>3</sub> <sup>2-</sup> (ppm)	<1	<1	<1	<1	<1	<1	-
Membrane filtrate	COD <sub>Mn</sub> (ppm)	<10	<10	<10	<10	<10	<10	800

[0206] From the results given in Table 5, it was found that when the pH value in the neutralization tank is 7 and higher, the concentration of Mn in membrane filtrate satisfies the effluent standard of 100 ppm and less.

[0207] The above is a description of the embodiments and working examples of the present invention. These embodiments and working examples have been described for ease of understanding of the present invention, and do not limit the scope of the present invention. All changes, modifications and additions obvious to a person skilled in the art of the invention described in the claims are embraced in the technical scope of the present invention.

## INDUSTRIAL APPLICABILITY

[0208] The present invention can provide a flue gas desulfurization method carried out by a wet lime-gypsum process in which sulfur oxide and nitrogen oxide in flue gas are absorbed and separated by using absorbent slurry of limestone or hydrated lime, a flue gas desulfurization system capable of properly carrying out the above-described method and a treatment method for the above-described absorbent slurry, and a method for effecting treatment for making waste water, which is discharged when sulfur oxide gas in combustion flue gas is desulfurized by the wet lime-gypsum process and especially by soot mixing desulfurization, nonpolluting.

**Claims**

1. A desulfurization waste water treatment method for treating waste water discharged from a wet type flue gas desulfurizer for absorbing and separating sulfur oxide in combustion flue gas by using a wet lime-gypsum process, wherein after hypochlorite is added to said waste water, the pH value is adjusted to 7 to 9.5, and said waste water is subjected to solid-liquid separation.
2. A desulfurization waste water treatment method for treating waste water discharged from a wet type flue gas desulfurizer for absorbing and separating sulfur oxide in combustion flue gas by using a wet lime-gypsum process, wherein after hypochlorite is added to said waste water, the pH value is adjusted to 7 to 9.5, and said waste water is subjected to solid-liquid separation after sulfite or bisulfite and a heavy metal chelating agent are added.
3. The desulfurization waste water treatment method according to claim 1 or 2, wherein said hypochlorite is added so that the oxidation-reduction potential is 600 mV and higher.
4. The desulfurization waste water treatment method according to claim 2, wherein said sulfite or bisulfite is added so that the oxidation-reduction potential is 200 mV and higher.
5. The desulfurization waste water treatment method according to claim 2 and 4, wherein the liquid to which said sulfite and bisulfite is added is agitated by air.
6. The desulfurization waste water treatment method according to claim 1 or 2, wherein said solid-liquid separation is microfiltration membrane separation.
7. The desulfurization waste water treatment method according to claim 6, wherein in said membrane separation, filtrate is agitated by air.
8. An absorbent slurry treatment method for treating absorbent slurry in which sulfur oxide gas in flue gas is absorbed, wherein after a mixing process in which a heavy metal chelating agent is added to and mixed with said absorbent slurry, there are provided a gypsum separation process in which gypsum is separated, an oxidation process in which an oxidizing agent is added to filtrate coming from said gypsum separation process, and a membrane separation process in which liquid coming from said oxidation process is filtrated by using a separation membrane.
9. An absorbent slurry treatment method for treating absorbent slurry in which sulfur oxide gas in flue gas is absorbed, wherein after a mixing process in which a heavy metal chelating agent is added to and mixed with said absorbent slurry in which sulfur oxide gas is absorbed in a desulfurization process, there are provided a gypsum separation process in which gypsum is separated, an oxidation process in which an oxidizing agent is added to filtrate coming from said gypsum separation process, and a membrane separation process in which treated liquid coming from said oxidation process is filtrated by using a separation membrane, and some of the liquid having been subjected to said gypsum separation process and oxidation process is returned to said desulfurization process as concentrate.
10. The absorbent slurry treatment method according to claim 8 or 9, wherein in addition to the processes described above, there are provided an activated charcoal adsorption process in which membrane filtrate subjected to said membrane separation process is brought into contact with activated charcoal and a fluorine adsorption process in which treated liquid coming from said activated charcoal adsorption process is brought into contact with a fluorine adsorption resin.
11. The absorbent slurry treatment method according to claim 8 or 9, wherein in said mixing process, said heavy metal chelating agent and a solidifying substance are added.
12. The absorbent slurry treatment method according to claim 8 or 9, wherein said heavy metal chelating agent is dithiocarbamic acid group or thiol group or both of them.
13. The absorbent slurry treatment method according to claim 8 or 9, wherein said oxidizing agent is hypochlorite.
14. The absorbent slurry treatment method according to claim 8 or 9, wherein the treated liquid-coming from said oxidation process is treated in a neutralization process in which a reducing agent is added, and then goes to said

membrane separation process.

15. The absorbent slurry treatment method according to claim 8 or 9, wherein a solid substance separated in said membrane separation process is returned to said mixing process, and sent to said gypsum separation process after being mixed with the absorbent slurry.
16. The absorbent slurry treatment method according to claim 10, wherein recycled waste liquid in said fluorine adsorption process is returned to said desulfurization process.
17. The absorbent slurry treatment method according to claim 14, wherein said reducing agent is a flue gas.
18. A flue gas desulfurization system comprising a desulfurizer for absorbing sulfur oxide gas in flue gas, a mixing tank in which a heavy metal chelating agent is added to and mixed with absorbent slurry coming from said desulfurizer, a gypsum separator for separating gypsum, an oxidation tank in which an oxidizing agent is added to filtrate from which gypsum is separated, and a membrane separation tank in which liquid coming from said oxidation process is filtrated.
19. The flue gas desulfurization system according to claim 18, wherein in addition to the elements described above, said flue gas desulfurization system comprises an activated charcoal adsorption tower in which filtrate coming from said membrane separation process is brought into contact with activated charcoal and a fluorine adsorption tower in which treated liquid coming from said activated charcoal adsorption tower is brought into contact with a fluorine adsorption resin.
20. The flue gas desulfurization system according to claim 18 or 19, wherein in said mixing tank, said heavy metal chelating agent and a solidifying substance are added.
21. The flue gas desulfurization system according to claim 18 or 19, wherein a neutralization tank in which a reducing agent is added to treated liquid coming from said oxidation tank is provided between said oxidation tank and membrane separation tank.
22. The flue gas desulfurization system according to claim 18 or 19, wherein said separation membrane is a tubular type microfiltration membrane, a submerged type flat-plate microfiltration membrane, or a submerged type hollow-fiber microfiltration membrane.
23. The flue gas desulfurization system according to claim 19, wherein said fluorine adsorption resin is a zirconium carrier type resin or a cesium carrier type resin.
24. The flue gas desulfurization system according to claim 18 or 19, wherein said membrane separation tank is installed in an absorption tower of said desulfurizer.
25. The flue gas desulfurization system according to claim 21, wherein said membrane separation tank and neutralization tank are installed in an absorption tower of said desulfurizer.
26. A flue gas desulfurization method using a wet lime process for treating flue gas containing sulfur oxide and nitrogen oxide, comprising an oxidation process in which the pH value of all or some of filtrate is adjusted to 3 to 4 and an oxidizing agent is added after some of absorbent slurry in a desulfurization process is extracted and gypsum is separated, a neutralization process in which an alkaline agent is mixed with said mixed liquid to adjust the pH value to 7 to 9.5, and a solid-liquid separation process in which the neutralized adjusted liquid is subjected to solid-liquid separation.
27. The flue gas desulfurization method according to claim 26, wherein after a heavy metal chelating agent is added to some of the absorbent slurry extracted from said desulfurization process, gypsum is separated.
28. The flue gas desulfurization method according to claim 26 or 27, wherein said oxidizing agent is hypochlorite.
29. The flue gas desulfurization method according to claim 26 or 27, wherein said solid-liquid separation is effected by membrane separation.

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30. The flue gas desulfurization method according to claim 26 or 27, wherein some of solid substance concentrate yielded by said solid-liquid separation is mixed with the absorbent slurry to be subjected to solid-liquid separation.
- 5 31. The flue gas desulfurization method according to claim 26 or 27, wherein some of solid substance concentrate yielded by said solid-liquid separation is supplied to an absorption tower as make-up water.
32. The flue gas desulfurization method according to claim 26 or 27, wherein filtrate subjected to said solid-liquid separation is discharged to the outside of the system as waste water.
- 10 33. The flue gas desulfurization method according to claim 26 or 27, wherein in said neutralization process, sulfite or sulfurous acid gas is added.
34. A flue gas desulfurization system using a wet lime process for treating flue gas containing sulfur oxide and nitrogen oxide, wherein on the downstream side of a gypsum separator for separating gypsum from absorbent slurry introduced from an absorption tower, there are provided an oxidation tank in which the pH value of all or some of filtrate from which gypsum has been separated is adjusted to 3 to 4 and an oxidizing agent is added, a neutralization tank in which an alkaline agent is mixed with the liquid coming from said oxidation tank to adjust the pH value to 7 to 9.5, and a membrane separation tank in which the liquid coming from said neutralization tank is subjected to solid-liquid separation by using a membrane.
- 15 20 35. The flue gas desulfurization system according to claim 34, wherein a mixing tank in which a heavy metal chelating agent is added to the absorbent slurry introduced from said absorption tower is provided, and said gypsum separator for separating gypsum is provided at the following stage of said mixing tank.
- 25 36. The flue gas desulfurization system according to claim 34 or 35, wherein said oxidation tank, neutralization tank, and membrane separation tank are arranged vertically as a unit under said gypsum separator so that fluid flows down from said gypsum separator to oxidation tank, from said oxidation tank to neutralization tank, and from said neutralization tank to membrane separation tank in succession.
- 30 37. The flue gas desulfurization system according to claim 34 or 35, wherein said oxidation tank, neutralization tank, and membrane separation tank are arranged vertically under said gypsum separator so that fluid flows down from said gypsum separator to oxidation tank and from said neutralization tank to membrane separation tank in succession.
- 35 38. The flue gas desulfurization system according to claim 34 or 35, wherein some of solid substance concentrate yielded by said solid-liquid separation is mixed with the absorbent slurry to be subjected to solid-liquid separation.
39. The flue gas desulfurization system according to claim 34 or 35, wherein some of solid substance concentrate yielded by said solid-liquid separation is supplied to said absorption tower as make-up water.
- 40 45 50 55 40. The flue gas desulfurization system according to claim 34 or 35, wherein filtrate subjected to said solid-liquid separation is discharged to the outside of the system as waste water.

FIG.1

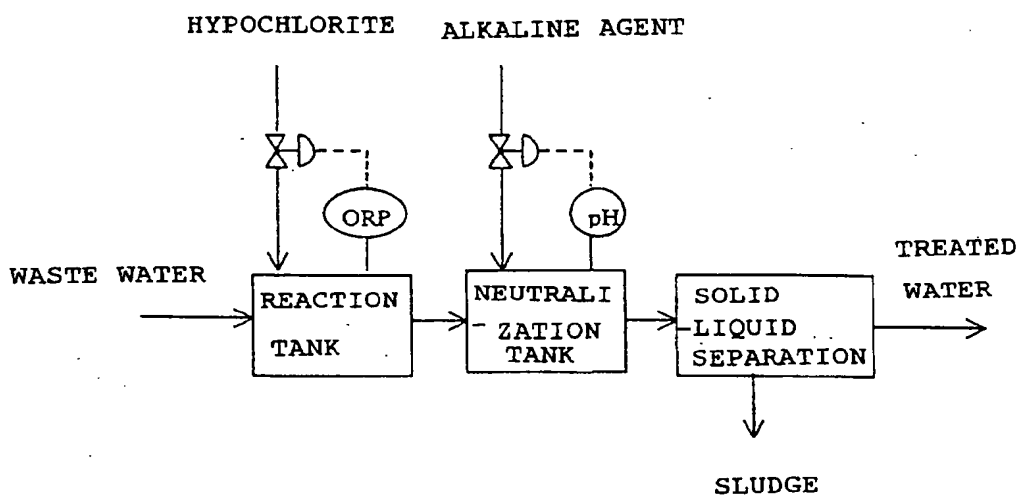


FIG.2

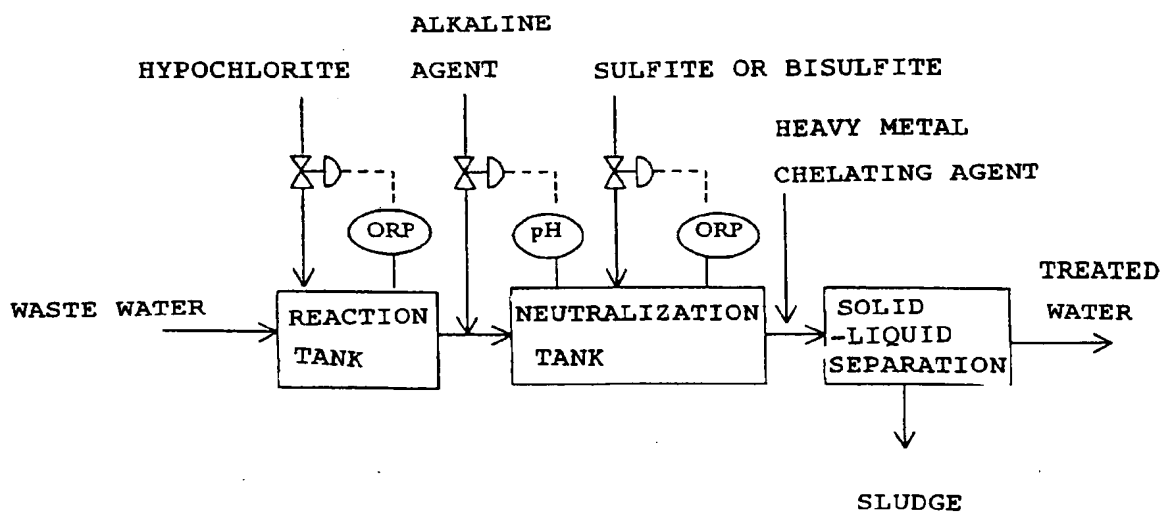


FIG.3

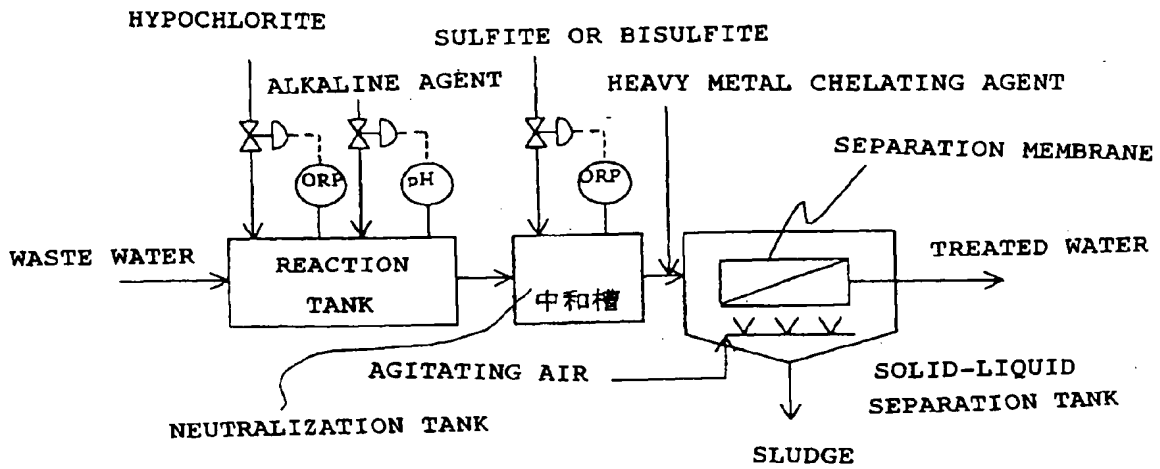


FIG.4

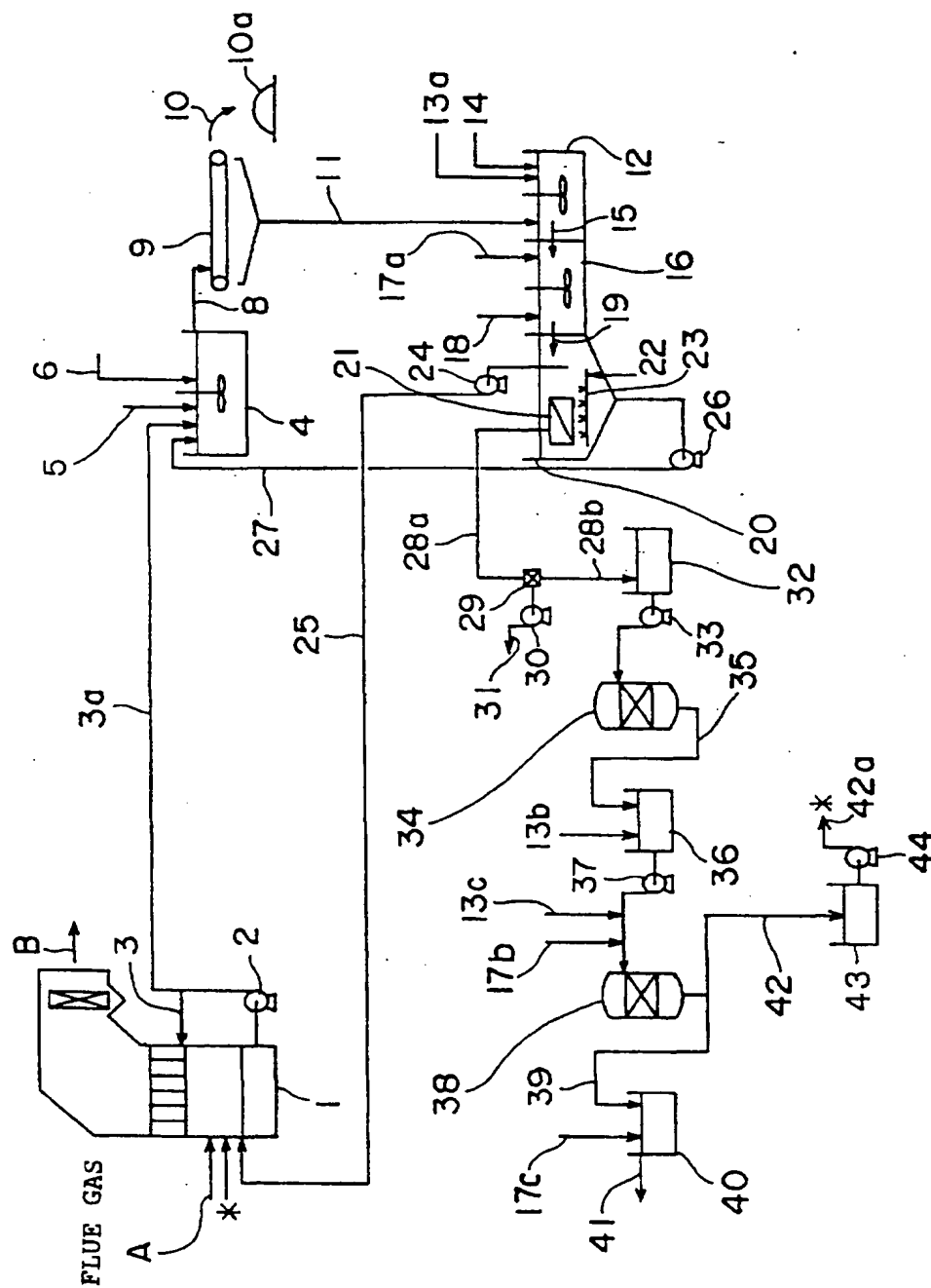


FIG.5

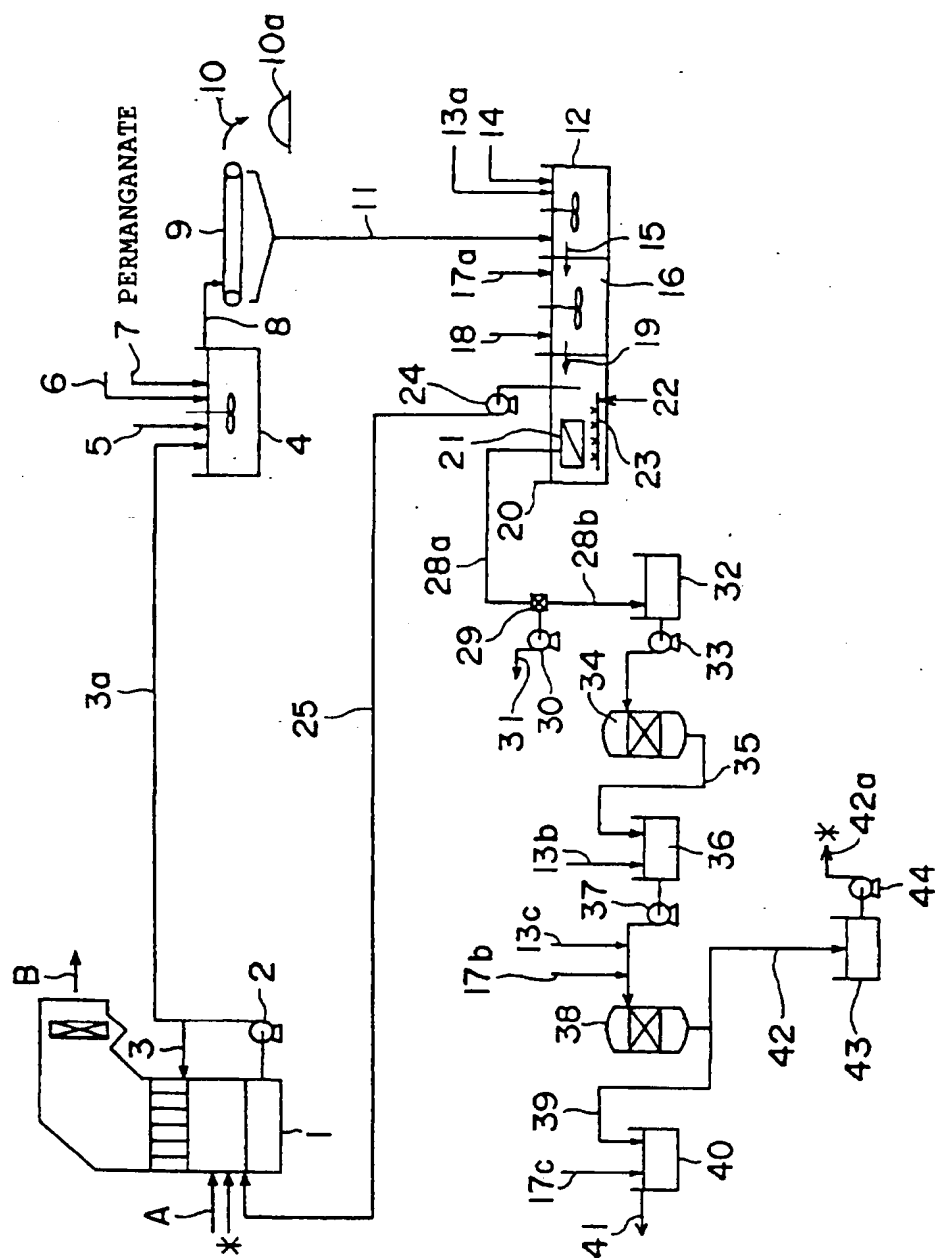


FIG.6

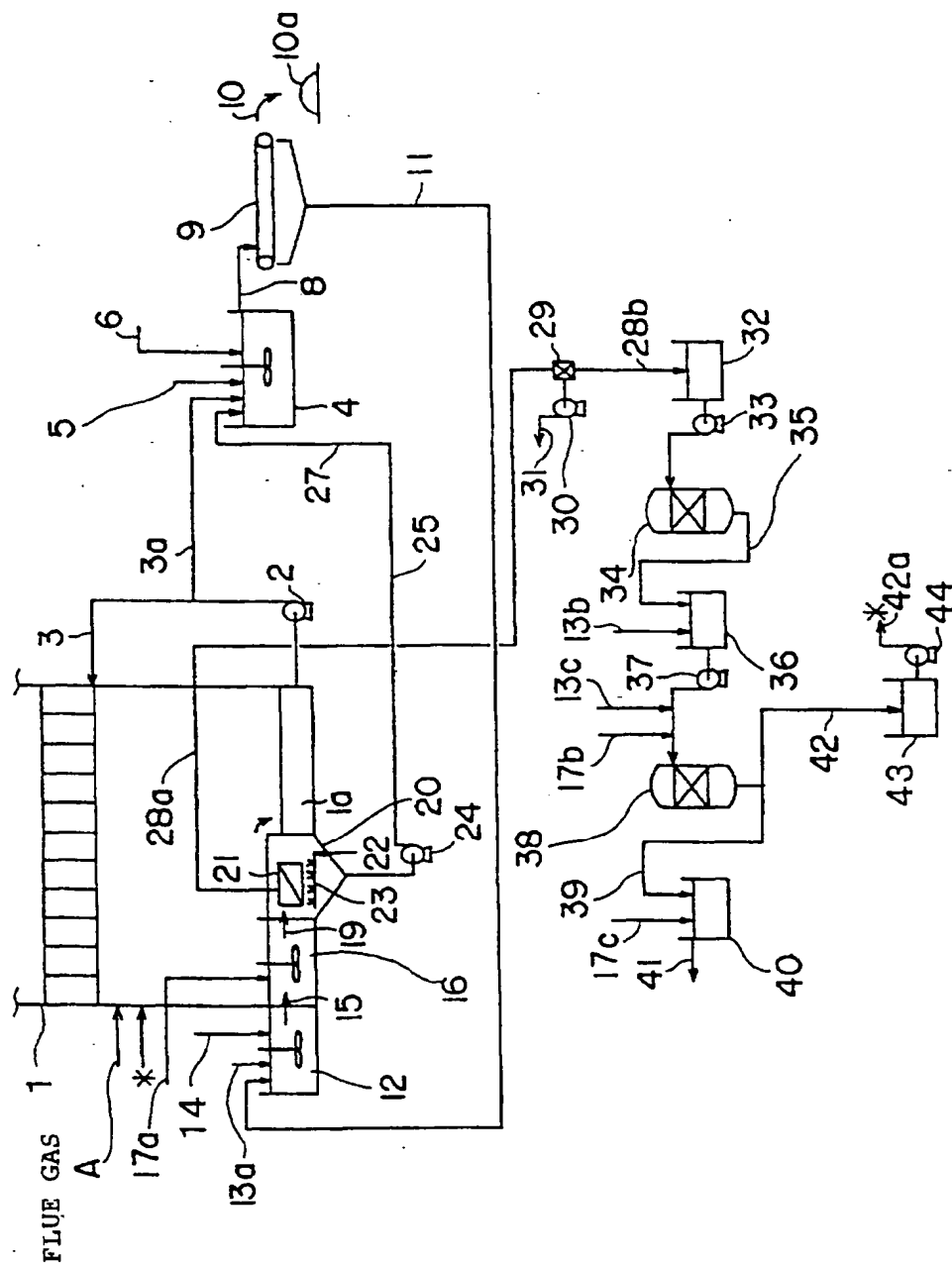


FIG.7

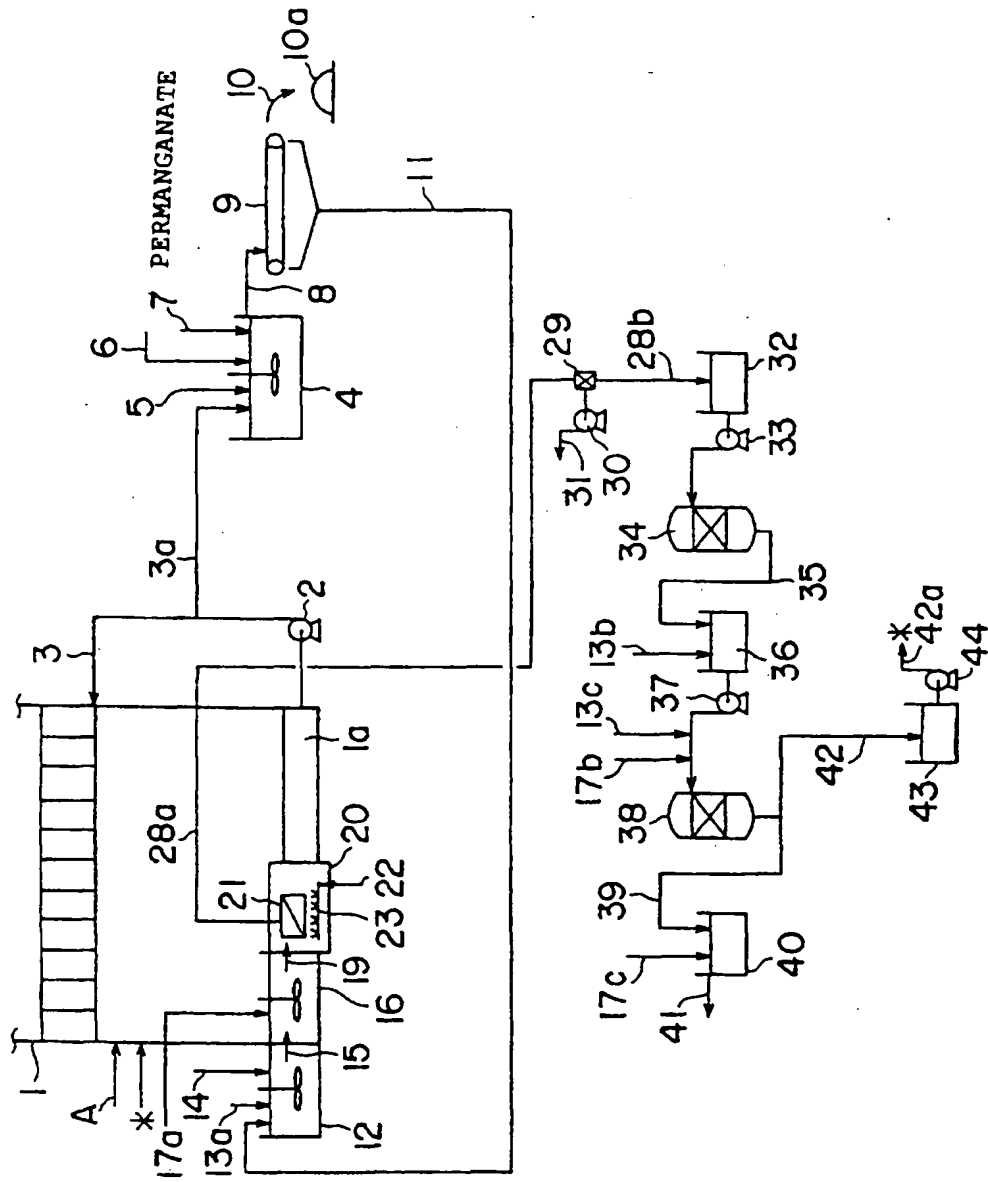


FIG.8

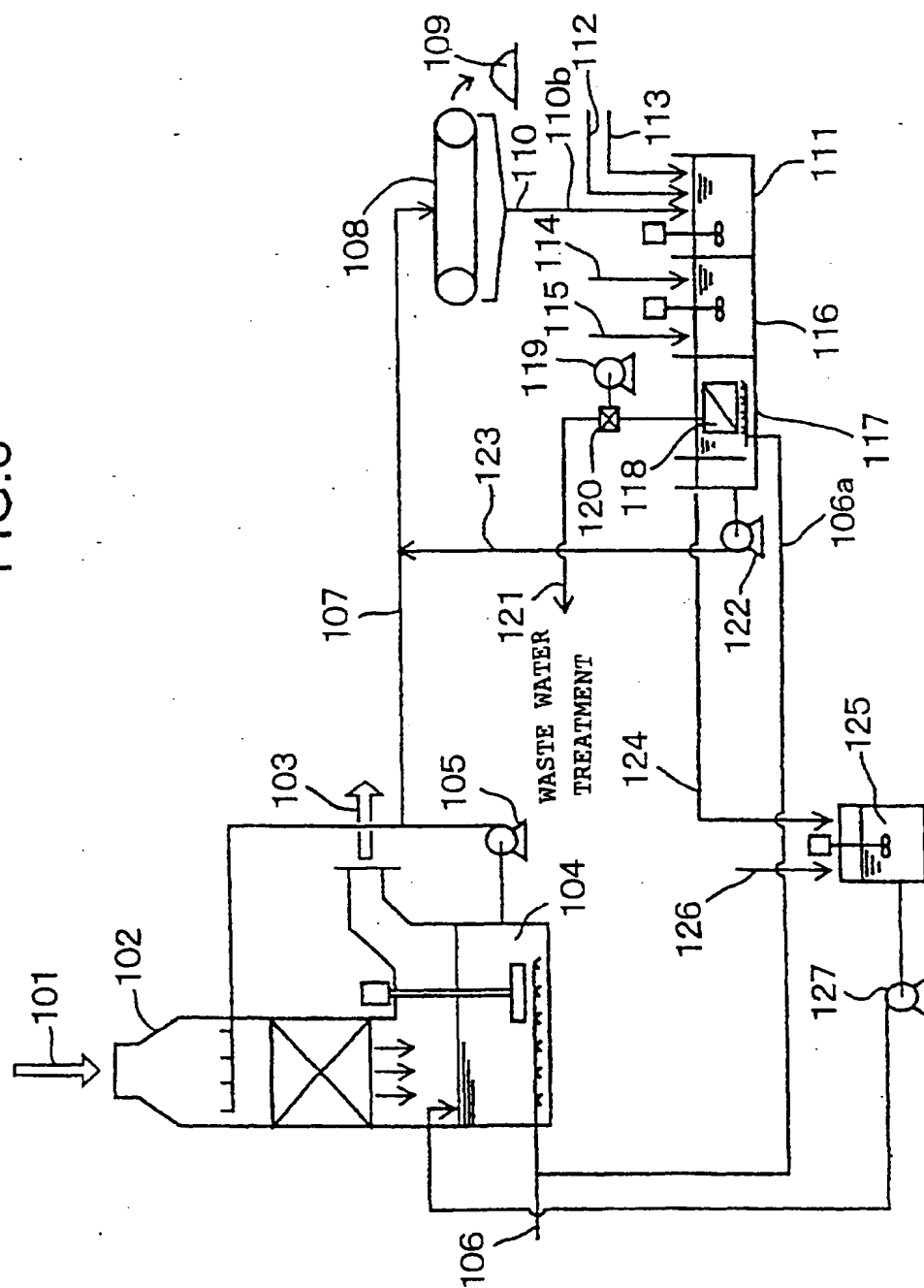


FIG. 9

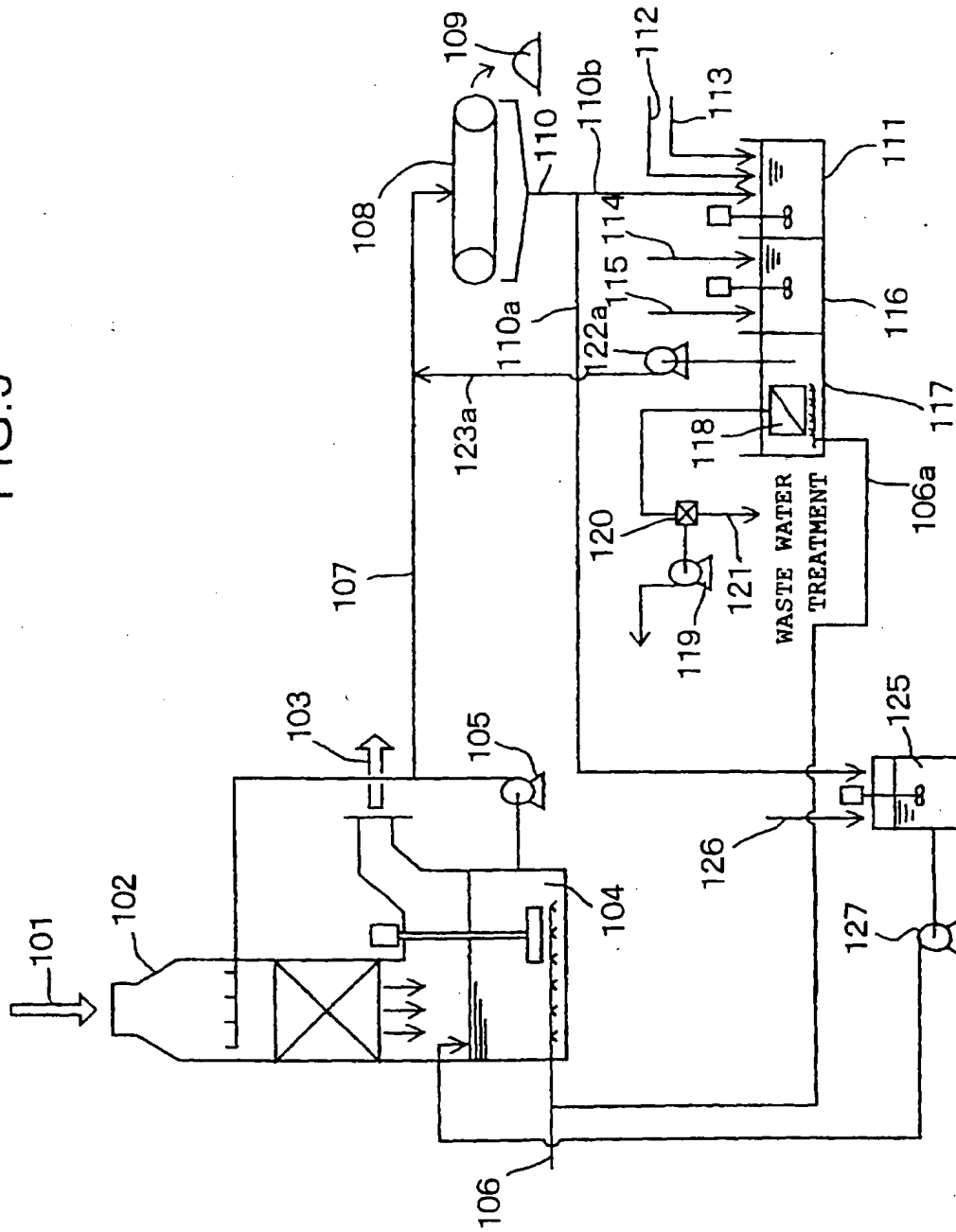


FIG.10

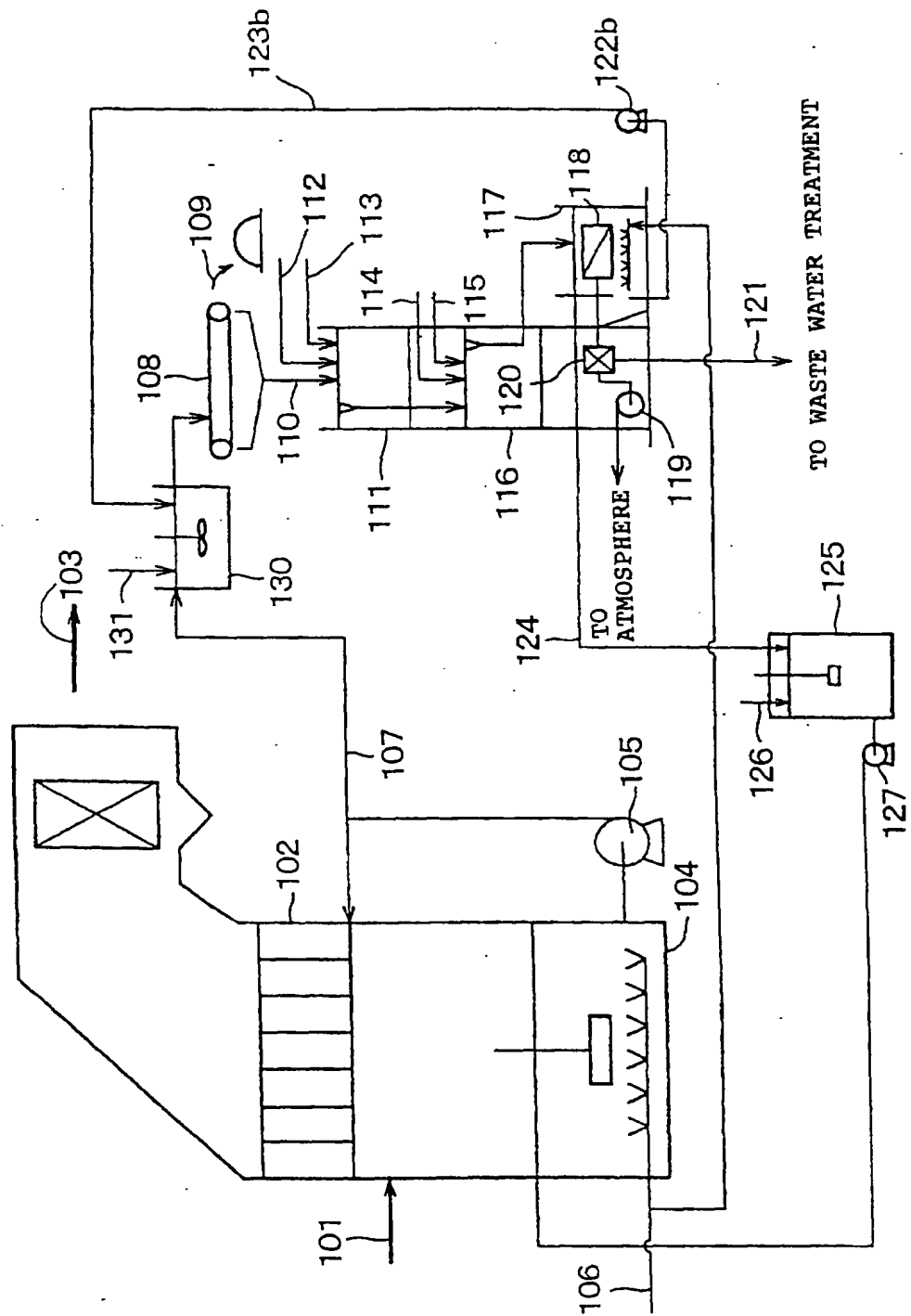


FIG.11

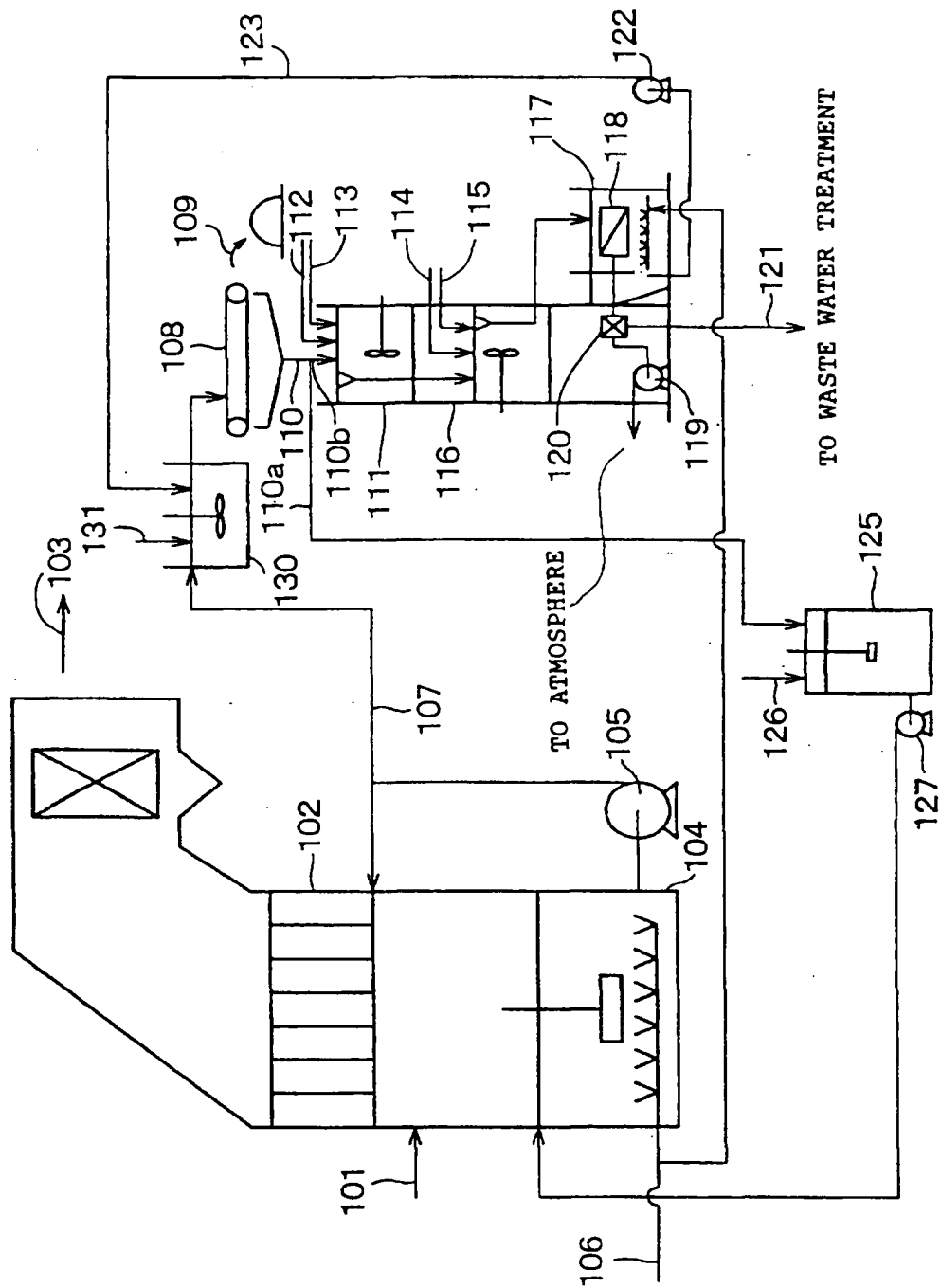


FIG. 12

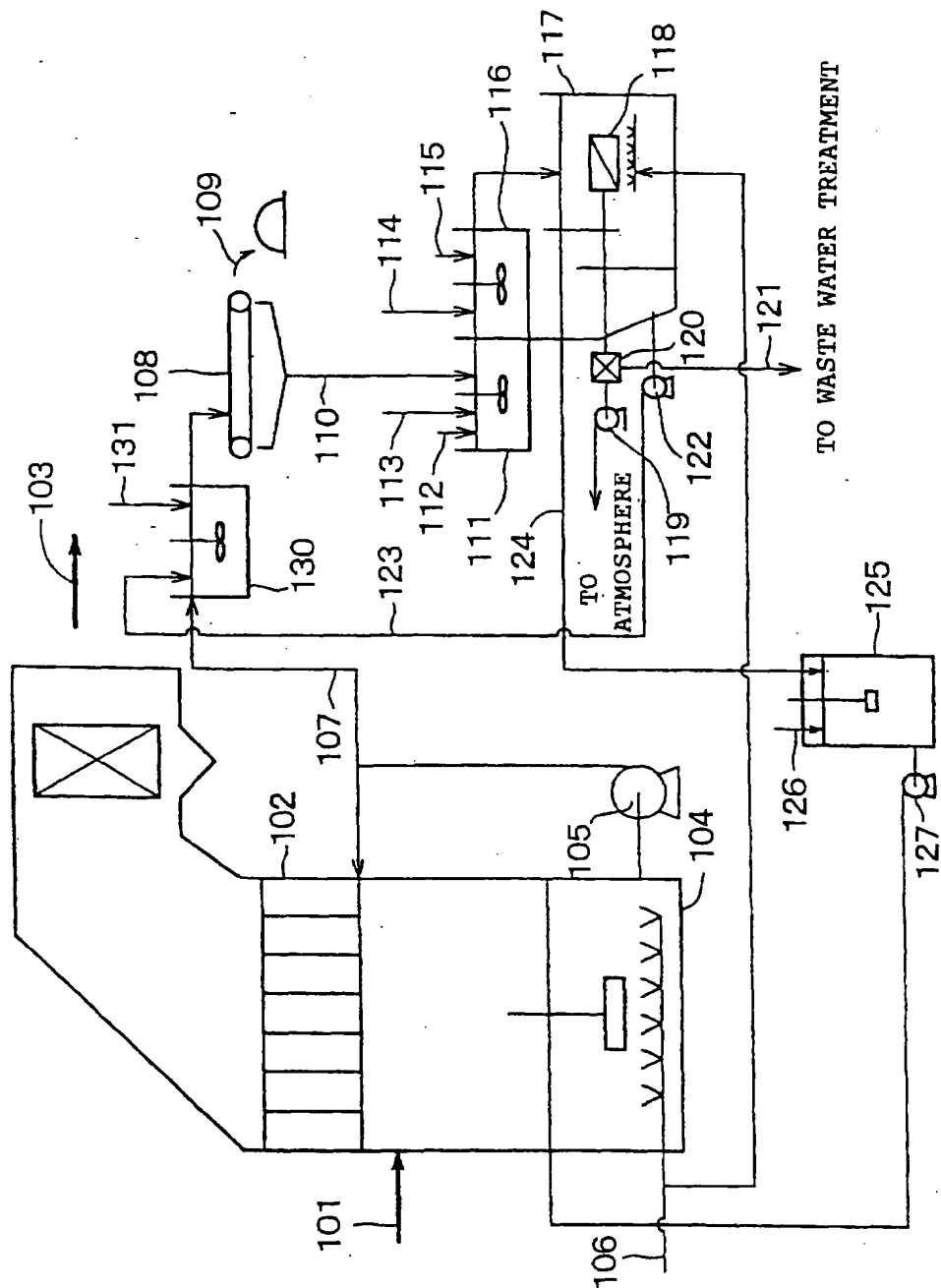
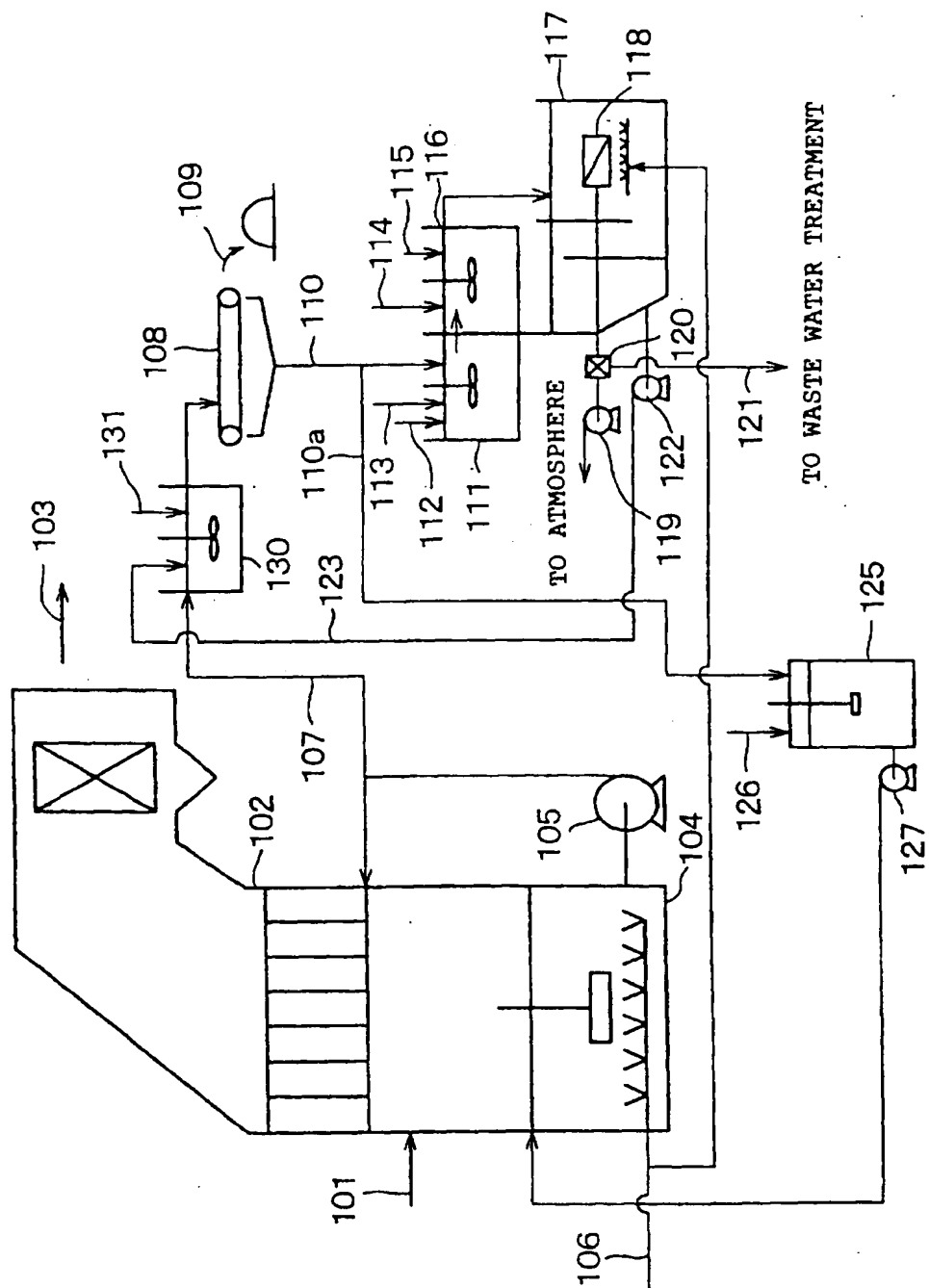


FIG. 13



## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP00/03093

A. CLASSIFICATION OF SUBJECT MATTER Int.Cl. <sup>7</sup> B01D53/50, C02F1/76, 1/62, 9/04		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) Int.Cl. <sup>7</sup> B01D53/34-53/85, C02F1/70-78		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Jitsuyo Shinan Koho 1926-1996 Jitsuyo Shinan Toroku Koho 1996-2000 Kokai Jitsuyo Shinan Koho 1971-2000 Toroku Jitsuyo Shinan Koho 1994-2000		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y A	JP, 9-29267, A (Tohoku Electric Power Company, Incorporated; Kurita Water Industries Ltd.), 04 February, 1997 (04.02.97), Claims; page 2, column 2, Par. No. [0010]; page 3, column 3, Par. No. [0019]; column 4, Par. Nos. [0028] to [0031]; page 4, column 6, Par. No. [0036] to page 5, column 7, Par. No. [0041]; Fig. 2 (Family: none)	1, 3, 6-7 2, 4-5, 8-16, 18-23, 26-35, 38-40 17, 24-25, 36-37
X	JP, 9-248576, A (Taiheiyo Kinzoku K.K.), 22 September, 1997 (22.09.97), Claims; page 2, column 1, Par. No. [0004]; Column 2, Par. Nos. [0009], [0010] (Family: none)	1, 3
Y	JP, 60-183091, A (Nkk Corporation), 18 September, 1985 (18.09.85), page 2, lower right column, line 15 to page 3, upper left column, line 6 (Family: none)	2, 4-5
Y	JP, 57-127487, A (Fujitsu Limited), 07 August, 1982 (07.08.82), page 2, upper left column, line 16 to upper right column, line 4 (Family: none)	2, 4-5
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
<p>* Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"I" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&amp;" document member of the same patent family</p>		
Date of the actual completion of the international search 08 August, 2000 (08.08.00)		Date of mailing of the international search report 22 August, 2000 (22.08.00)
Name and mailing address of the ISA/ Japanese Patent Office		Authorized officer
Facsimile No.		Telephone No.

Form PCT/ISA/210 (second sheet) (July 1992)

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP00/03093

**Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)**

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:  
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

**Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)**

This International Searching Authority found multiple inventions in this international application, as follows:

Claims 1, 2, 8, 9, 18, 26 and 34, all of them being independent claims, have been checked as to whether they comply with the requirement of unity of invention or not.

Claims 1, 2, 26 and 34 are common in that a flue gas desulfurization drain water (or a filtrate after separation of gypsum from a slurry formed by absorption) is added with a hypochlorite (or an oxidizing agent), is adjusted to have a pH of 7 to 9.5, and then is subjected to solid-liquid separation. This common technical matter appears to correspond to "special technical features" provided by PCT Rule 13.2 (ii), and hence there is a technical relationship involving "special technical features" among the inventions of claims 1, 2, 26 and 34. Accordingly, the inventions of claims 1, 2, 26 and 34 are a group of inventions so linked as to form a single general inventive concept provided by PCT Rule 13.1.

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest ☐ The additional search fees were accompanied by the applicant's protest.  
☐ No protest accompanied the payment of additional search fees.

Form PCT/ISA/210 (continuation of first sheet (1)) (July 1992)

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP00/03093

## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
PY	JP, 11-137958, A (Mitsubishi Heavy Industries, Ltd.), 25 May, 1999 (25.05.99),	8-16,18-23
PA	Claims; especially, Claims 1,2,8,9; page 4, Par. Nos. [0013], [0015] & KR, 99029232, A	17
Y	JP, 7-75778, A (Kurita Water Industries Ltd.), 20 March, 1995 (20.03.95), Claims; page 2, column 2, Par. No. [0013]; page 3, column 3, Par. Nos. [0020] to [0021]; Fig. 1 (Family: none)	8-16,18-23
Y	EP, 465439, A1 (MITSUBISHI JUKOGYO KABUSHIKI KAISHA), 08 January, 1992 (08.01.92),	26-35,38-40
A	Claims; Fig.2 & JP, 4-59026, A & US, 5284557, A & DE, 69111927, E	36-37

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP00/03093

Continuation of Box No.II of continuation of first sheet(1)

On the other hand, claims 8, 9 and 18 do not have the constitution that a pH is adjusted to a value of 7 to 9.5, and thus have the common constitution with other claims only in the procedure wherein a filtrate is added with an oxidizing agent and then is subjected to solid-liquid separation among the above-mentioned common technical matters. However, since the procedure wherein a filtrate is added with an oxidizing agent and then is subjected to solid-liquid separation (hereinafter referred to as the common procedure) is a technique having been well known before the present application and thus the common procedure does not appear to be a technical feature disclosing the contribution to the prior art, the common procedure does not conform to "special technical features" provided by PCT Rule 13.2 (ii). Therefore, inventions of claims 1, 2, 26 and 34 and those of claims 8, 9 and 18 do not appear to comply with the requirement of unity of invention.